

THEORY OF VALENCY IN PROGRESS



EDITED BY V. I. KUZNETSOV

Mir Publishers · Moscow

This monograph discusses on the central problems in modern chemistry, the theory of valency and its development. The authors describe the present state of the problem and make an endeavour to predict its prospects. The book is intended for a wide circle of readers, chemical researchers, and engineers, students and teachers in higher schools and colleges.

VLADIMIR KUZNETSOV, the editor of this book and the author of its opening and concluding chapters, is an active member of L'Academie Internationale d'Histoire des Sciences [Paris]. He is the Head of Department at the Institute for Study of History of Natural Sciences and Technology and a professor at Medeleev's Chemical and Technological Institute in Moscow. Prof. Kuznetsov is the author of several monographs dealing with the problems of catalysis, chemistry of polymers, and chemistry of organometallic compounds. He is the author of "Dialectics of Development of Chemical Science" and "The Trends in Development of Chemistry", where he has proposed an original theory of development of chemical sciences and substantiated their homological, or hierarchich classification,



РАЗВИТИЕ УЧЕНИЯ О ВАЛЕНТНОСТИ

Под редакцией
доктора химических наук
В. И. КУЗНЕЦОВА

THEORY OF VALENCY IN PROGRESS

Edited by
V. I. Kuznetsov

*Translated from the Russian
by Alexander Rosinkin*

Mir Publishers Moscow

First published 1980

Revised from the 1977 Russian edition

.

На английском языке

© Издательство «Химия», 1977

© English translation, Mir Publishers, 1980

Contents

Foreword	9
 Chapter 1. The Modern State of the Problem (V. I. Kuznetsov)	
1. The Evolution of the Concept of Chemical Bond and the Problem of Valency	12
2. Valency: Is It the Property of a Free or a Bound Atom?	23
3. What Are the Objects of the Theory of Valency?	26
4. Can Valency Be Characterized by Numbers Other Than Whole?	28
5. Valency and Atom Reactivity	30
References	31
 Chapter 2. The Evolution of the Theory of Valency (M. G. Fayershtein)	
1. Formation of the Concept and Theory of Valency	35
2. The History of the Word "Valency"	44
3. The History of the Term "Chemical Bond"	48
4. Relationships Between the Concepts of Chemical Bond and Valency	50
5. Butlerov's Contribution to the Development of the Theory of Valency	52
6. The History of Notation in the Theory of Valency and Chemical Bond	53
7. First Attempts of Theoretical Explanation of the Nature of Valency and Its Regularities	57
8. The Problem of Constant and Variable Valency	63
9. Relationships Between the Concepts of Valency, Chemical Affinity, Chemical Bond, and Chemical Structure	68
References	72

Chapter 3. Development of the Valency Concept in the Aspect of the Theory of Periodicity (A. A. Makarenya)

1. Relationships Between Valency and Other Properties of Elements According to Mendeleev	75
2. Valency and Relationships Between Forms of Compounds	76
3. Valency and Elements Position in the Periodic System	77
4. Mendeleev's Attitude Towards Valency	81
References	84

Chapter 4. The Theory of Valency and the Coordination Theory (Yu. I. Solovyov, P. I. Staroselsky)

1. Hypothesis of Constant Valency and Its Criticism	85
2. Valency Problem from the Aspect of Mendeleev's Periodic Law	95
3. "Residual Affinity" of Atoms	96
4. Spatial Concepts and the Theory of Chemical Affinity and Valency	99
5. Werner's Model of Carbon Atom	101
6. Coordination Theory of Werner	102
7. Main and Auxiliary Valencies	106
8. Electronic Theories of the Structure of Complex Compounds	111
References	116

Chapter 5. Formation of Spin-valency Theory (I. S. Dmitriev, S. G. Semyonov)

1. Formal-physical Interpretation of the Valency Concept in Pre-quantum-mechanical Electron Theories	119
2. The Emergence of the Mathematical Apparatus of the Spin-valency Theory (19th-early 20th century)	127
3. The Valency Concept in the Valence Bond Method	130
References	135

<i>Chapter 6.</i>	Manifestation Forms of Atom Valency Potentialities (R. B. Dobrofin)	
	1. Valency as Empirical Invariant of Atom Properties	137
	2. Electronic Interpretations of the Valency Concept	140
	3. Dependence of Forms of Valency Potentialities on the Electron Structure of Free Atoms	146
	References	148
 <i>Chapter 7.</i>	 Molecular-orbital Theory of Valency (S. G. Semyonov)	
	1. The Concept of Chemical Bond Multiplicity in the LCAO Method	151
	2. Quantum-chemical Interpretation of Valency	156
	3. Valency Structure of Organic Compounds	163
	4. Conclusion	168
	References	169
 <i>Chapter 8.</i>	 Dynamic and Cooperative Processes of Electron Density Redistribution and the Valency Problem (S. P. Ionov, G. V. Ionova)	
	References	179
 <i>Chapter 9.</i>	 Comparative Assessment of the Main Quantum-chemical Methods (N. P. Borisova)	
	1. Main Quantum-chemical Approximations	182
	2. Mathematical Principles of the MO and VB Methods. Non-empirical Calculations	187
	3. Special Features of Semi-empirical MO (LCAO) and VB Methods	197
	References	208
 <i>Chapter 10.</i>	 Hypervalent Bonds in Coordination Compounds of the Main Sub-group Elements (D. V. Korolkov)	
	1. Special Features of Electron Structure of Coordination Compounds of Non-transition Elements	210
	2. Hypervalent Bond Model	216
	3. Chemical Consequences of Hypervalent Bond Model	222
	References	230

Chapter 11. **The Results of the Historico-logical
Analysis of the Valency Problem
(V. I. Kuznetsov)**

1. General Tendencies in the Development of the Theory of Valency	232
2. Valency as a Reactive Power of an Isolated Atom	234
3. Valency as the Structural Characteristics of the Atom in a Molecule	245
4. "Free Valencies" of Atoms in Molecules	248
5. Valency Theories	250
References	258

Foreword

It is difficult to overestimate the role which the theory of valency has played in the development of chemical science. It has become an indispensable link between the mysterious "combining weights" and the whole numbers in Dalton's law of multiple proportions. The theory of valency has explained one of the oldest and the most obscure chemical concepts, the concept of affinity, and laid a straight way to the theory of chemical structure. It was no less significant in the formation of the theory of periodicity and the atom structure. Moreover, the theory of valency turned out to be a kind of a methodological key to the treasure-house of chemical knowledge. Chemical teachers maintain that it is practically impossible to make the first steps in chemistry without using the valency concept.

However the present situation in theoretical chemistry is very complicated. Recent advances in structural chemistry show that the classical theory of valency fails to interpret many of the newly discovered chemical facts. The number of such "unexplainable" facts is steadily increasing, and many chemists think that the classical theory of valency is untenable in general. Scientists speak out different views and some of them run to extremes. Many scientists come to full negation of valency, as the concept which has lost its former importance, while others, on the contrary, widen its scope to incorporate into it recent data on the molecular structure.

Time will show who of them is right, but time is a precious factor of human activity and it should be handled with great care, especially so when we deal with such an important and urgent problem as the problem of valency. The importance of the valency problem is determined by its central position in the entire modern theoretical chemistry, and whatever we mean by valency, it always implies the reactivity of free atoms, its realization in the form of chemical bonding, the structure of chemical compounds, and finally the energy aspects and the reactivity of chemical substances. It is therefore very important for the modern theoretical chemistry to give as full definition of valency as possible.

The problem of the valency concept is no less important for chemical teachers either. The teacher must give his students the information concerning all main discoveries and theoretical ideas in

chemistry, including those extending beyond the framework of the classical theories. At the same time it is always easier to conceive a new idea rather than to revise and learn anew the old one. And the situation is especially difficult when it concerns such fundamental concepts as valency.

We think it necessary to emphasize that in our approach to the solution of the valency problem, we do not rest ourselves on any single (even "most objective") standpoint. On the contrary, each theoretical opinion, however it relates to all other standpoints, is regarded by us as a factual material objectively reflecting the evolution of the valency concept. This material is thus the starting empirical point in our discussion of the problem. And although we assess the past events in the light of present developments, our criterion for the determination of the essence of the valency concept is the *entire* evolution of the concept on the whole. And from this standpoint we can assess not only the present status of the problem but also, in a certain extent, predict future developments. It should also be noted that any definition of valency is only one of the numerous links in the chain of continuous changes in what we understand by valency. Therefore we think that the best definition of any phenomenon is the one which is derived from the analysis of its evolution.

As we discussed the theory of valency, we, naturally, proceeded from the simple to the complex. And while the first six chapters can easily be understood by pupils of the secondary school, further discussion is addressed to a more advanced reader. The concluding chapter is actually a brief review of all known theories of valency given in the general form. But the entire book will undoubtedly be helpful to scientists, engineers, teachers, and students who devoted themselves to chemistry.

We take the opportunity to express our deep gratitude to S. A. Shchukarev for his useful advice and discussion in the process of preparing the manuscript.

Chapter One The Modern State of the Problem

Both classical and modern chemistry treat of valency as of “the property of an atom of a given element to combine with or substitute for a definite number of atoms of another element” [1]. This definition is cited from the Chemical Encyclopedia (1961) and in this form it is quoted in textbooks of chemistry for higher school [2, 3]. Valency is regarded as a quantitative measure of properties of elements (expressed in whole numbers) whose criterion is the “number of chemical bonds formed by an atom in the formation of chemical compounds” [2]. To explain valency, the authors would usually resort to quite illustrative and comprehensible examples of empirical formulas of inorganic compounds. For example, the “Course in General Chemistry” by Menshutkin which went out in four editions late in the 1920s and early 1930s (i.e. before the foundation of quantum chemistry) reads as follows [4]: “An atom which combines with two atoms of hydrogen is characterized by two valency units; that combining with three hydrogens, by three valency units; with four by four units.... Valency of an element can be determined against any other chemical element whose valency by hydrogen is known, e.g. against univalent chlorine, divalent oxygen.... With respect to oxygen, some chemical elements are hepta- and octavalent, which is evident from the following comparison of compounds and types of oxygen-containing compounds:

Compound	Na ₂ O	CaO	Al ₂ O ₃	CO ₂	P ₂ O ₅	WO ₃	Mn ₂ O ₇	OsO ₄
Type	R ₂ O	RO	R ₂ O ₃	RO ₂	R ₂ O ₅	RO ₃	R ₂ O ₇	RO ₄
Atom valency	1	2	3	4	5	6	7	8

Over 40 years have passed since this textbook was published and radical changes took place in the views on the ways, by which chemical bonds are realized in inorganic compounds, and on the very nature of chemism, but the modern courses in chemistry intended for higher school describe valency using the same old criteria. For example, the “Course in Chemistry” published in 1971 reads: “Titanium combines with chlorine to give the following compounds: TiCl₂, TiCl₃, and TiCl₄, in which the valency of titanium is +2, +3, and +4” [2].

Such a view on valency and its criteria ("number of chemical bonds") persists not only in textbooks but in scientific literature as well [5-8], although in the latter these criteria are, of course, coordinated with the theory of periodicity and hence with the data on the electron configuration of atoms. But calculations of the number of chemical bonds, which a given atom forms, is often erroneous and the valency which is given to the element is often arbitrary. Firstly, the empirical formula of most inorganic compounds does not in itself give any information on the "number of chemical bonds", because particles of compounds, for example of those given in the above examples, are not as a rule monomeric molecules but di- or trimeric crystal polymers with multicentre bonds. Secondly, even monomeric molecules often form bonds that are quite different from those that could be expected from the empirical formula. In this connection the criteria of valency should be revised, and this means that our views on the valency itself should be substantially changed.

In our next paragraph we shall describe in more detail the conflict between the old but still alive views on valency and the modern theory that arose from advances made in the study of the chemical bond.

1. The Evolution of the Concept of Chemical Bond and the Problem of Valency

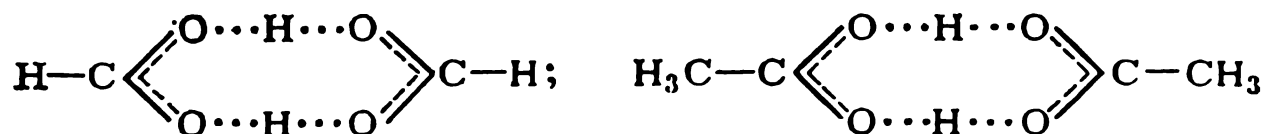
The collision between the old and the modern theory of valency arises mainly from the changes in our views on the chemical bond that took place firstly as a result of using physical methods in the study of the structure of compounds, and secondly because of the extension of quantum mechanics onto chemical objects. We shall discuss these two facts, and shall begin with the "perturbation" that the physical methods of investigation brought about into the study of valency.

Hydrogen Bond. Since the time when Kekulé offered his theory of valency, the classical chemistry used a "typical" monovalent hydrogen as a standard of valency. What made the scientists choose hydrogen as the standard was the "invariable" property of its atom to form only one bond with the atoms of any other element, H—I, H—Cl, H—OH, H—OCH₃, H—CN, H—OC₆H₅. Now everyone knows that the nature of this bond differs significantly in various compounds and is characterized by different energies (kcal/mole) [9]:

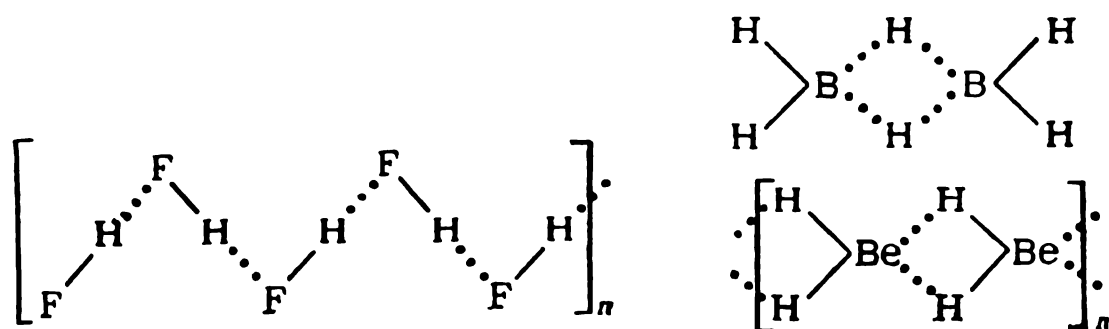
H—H	H—F	H—Na	H—C(CH ₃) ₃	H—C(C ₆ H ₅) ₃	H—Hg
103.2	134.0	47.0	80.0	14.0	8.6

This fact alone makes the investigator wonder, what stands for this valency dash, which was formerly considered to be the unit of

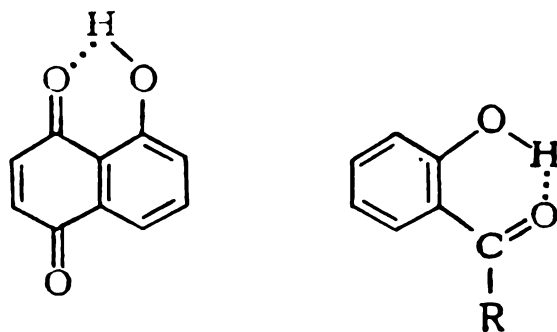
chemical bond formed by the mutual saturation of two affinity units. The modern scientist knows something else. Using diffraction methods, calorimetric measurements, infra-red spectra, electron paramagnetic resonance, we have established that the hydrogen atom can form not only one bond with the atoms of other elements, but also two bonds. For example, in formic acid, which has a dimeric form even in the gaseous state, and also in acetic acid, whose dimeric form is less stable, the atom of hydrogen is bonded with two oxygen atoms:



Such a bond, which is known as the hydrogen bond, is not characteristic of oxygen-containing compounds alone [5, 10]; hydrogen forms two bonds with many other elements as well:



The energy of the hydrogen bond is as high as 20 and even 30 kcal/mole in some compounds, i.e. this bond proves to be stronger than the C—H bond in triphenylmethane. Quasi-aromatic compounds



are another example of compounds with especially strong bonds.

By the present time we have ample and varied information on the hydrogen bond in water, crystal hydrates, aqueous and alcoholic solutions, aromatic and quasi-aromatic systems, carbohydrates, fats, and proteins [10]. This information indicates that the hydrogen bond is extraordinarily widely spread and this adds something quite new to our concepts not only of the valency standard but of the valency itself as well.

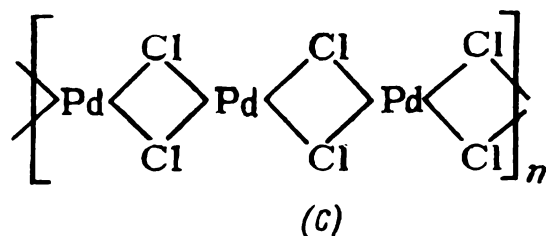
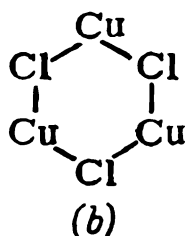
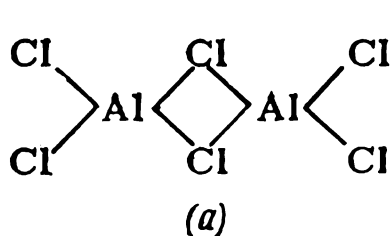
Chemical Bonds in Inorganic Compounds. The study of the structure of solid inorganic compounds by physical methods changed our views on valency even stronger. The known Soviet specialists in chemistry of crystals, Bokiý and Belov, indicate that the results of the earliest (1920-1930) X-ray structural investigations showed that "crystals of most inorganic substances, for example minerals, have no atom grouping which could be called molecules. This conclusion was unexpected to chemists which would assume matter to be constructed of molecules" [11]. It is quite clear that this conclusion could not but produce its effect on the concept of valency.

At the present time not only X-ray methods are used to study inorganic compounds, but also the methods of diffraction of neutrons and electrons, and infra-red spectrophotometry; the scientists study spectra in the visible and the ultra-violet regions, combination scattering spectra, they also use methods of nuclear magnetic resonance, electron paramagnetic resonance, and nuclear quadrupole resonance [12-14]. As a result, a new field of science arose—crystal chemistry, it gives information on the structural chemical regularities of formation of crystal lattices [15].

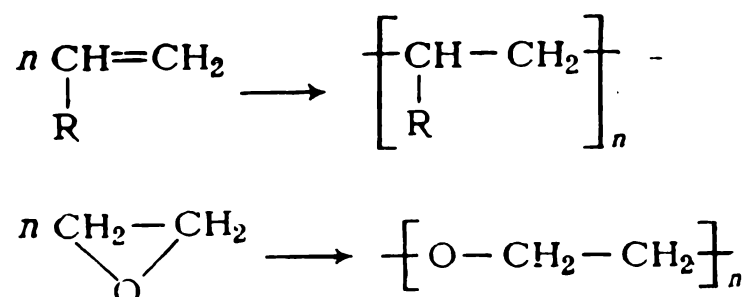
One of the main achievements in modern crystal chemistry is drawing a distinct boundary line between organic and inorganic compounds. Almost 100 per cent of organic compounds are of molecular type in all states, i.e. they are substances consisting of molecules, whereas more than 95 per cent of inorganic compounds are of non-molecular type. In other words, the minutest particles of most inorganic compounds are not molecules but single crystals, kind of polymers of the atomic aggregation which is designated in classical chemistry by the empirical formula.

To illustrate this "polymer" state of inorganic substances let us consider, for example, such simple and well-known inorganic compounds as metal chlorides. Like hydrogen, chlorine was also used as a standard of valency in classical chemistry. It was considered to be only univalent in compounds with metals, because it forms only one bond with metal atoms. As we have already said, the authors of the recently published "Course in Chemistry" [2] chose chlorine to illustrate valencies +2, +3, and +4 in compounds MeX_2 , MeX_3 , and MeX_4 . But crystal chemistry shows that in metal compounds chlorine forms as a rule not one but several bonds.

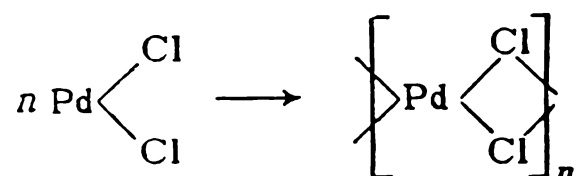
Metal chlorides of dimeric (a), trimeric (b), and polymeric (c) character [5, 16] occur frequently:



These inorganic polymers substantially differ from organic ones which (in polymerization reactions) are thought to be formed as a result of opening and releasing of multiple bonds or ring bonds:



For this reason, the valency of the component elements, if it is not determined by the number of bonds, remains generally speaking the same as in the monomers. The formation of inorganic polymers is different. As the diagram below shows



the number of bonds formed by palladium atom and chlorine atom is doubled. This might suggest that the valency of these elements is doubled as well. Moreover, the differences between organic and inorganic polymers are even deeper. Some inorganic polymers cannot exist in the monomer state, and even when in the gas state, they are dimers, trimers, etc. For example, gaseous cuprous chloride is not CuCl but a cyclic compound (b) [17]. The study of the quadrupole cleavage in the spectra of inorganic tin compounds reveals that tin tetrafluoride cannot have monomeric tetrahedral structure. It is an octahedron with two bridge atoms of fluorine [13].

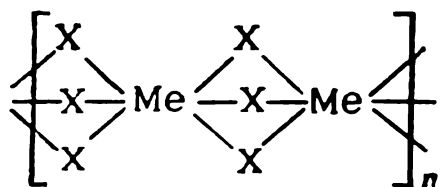
The number of bonds formed by the halogen atoms in the trimeric crystalline lattice of metal chlorides (halides) is as a rule even greater. For example, in the cubic lattice of NaCl , each sodium atom is bonded with six chlorine atoms (NaCl_6), and each chlorine atom with six sodiums (Na_6Cl). The structural formula of this compound is therefore $[\text{NaCl}_{6/6}]^{3\infty}$. This formula indicates that the coordination number of both elements is six, while the symbol “ 3∞ ” indicates that the atomic aggregation repeats to infinity in all three directions.

One could expect that the analogue to sodium chloride, cesium chloride, might have the same structure. But the ratios of ionic radii of cesium and chlorine are different (a geometric factor in itself) and the crystal lattice changes here into a body-centred one,

where each cesium is connected with eight chlorine atoms and each chlorine atom with eight atoms of cesium: $[\text{CsCl}_{8/8}]^{3\infty}$. This means that the formulas of each separate cesium chloride complex should be written as CsCl_8 for cesium and Cs_8Cl for chlorine.

The crystalline forms of non-linear "polymers" MeCl_2 and MeCl_3 are no less complicate. For example, TiCl_2 is a crystalline compound having a hexagonal lattice. The compound TiCl_3 has four crystalline modifications, of which only one is a linear polymer, while TiCl_4 is a monomeric compound. It follows that if we admit that the criterion of valency is the "number of bonds formed by an atom of a given element", chlorine is univalent only in TiCl_4 , where titanium is tetravalent. In other compounds chlorine is divalent, hexavalent, and even octavalent. The valency of titanium in TiCl_2 and TiCl_3 is twice as high as in TiCl_4 .

Using the methods of electron paramagnetic resonance and nuclear quadrupole resonance the scientists found (in the 1960s) that many metal halides of the type MeX_3 are so constructed that the halogen atoms act like bridge elements in the structure of compounds, e.g. [13]:



The structure of CrCl_3 is a distorted octahedron where each chromium atom is surrounded with six chlorines, and each atom of chlorine is placed between two chromium atoms. Ferric chloride, having the empirical formula FeCl_3 , has a similar structure. Syrkin states therefore that "we cannot maintain that chlorine is univalent and iron trivalent in FeCl_3 , because the number of bonds formed by each of these atoms with its neighbours is quite different. The concept of "tervalent iron" is out-of-date, because iron does not form three bonds... We have no "tervalent iron" in an aqueous solution of FeCl_3 either, because the atom is coordinated with six molecules of water" [16].

These examples, whose number can easily be extended, indicate the crisis in the classical definition and in the concept of valency itself. In the overwhelming majority of inorganic compounds, because of their peculiar polymeric character, the "number of bonds" does not agree with the accepted measure of valency and cannot therefore be the criterion of this measure.

The valency problem becomes even more critical if we remember that the crystal chemical structure of compounds in their ideal aspect was discussed here, while in reality all crystals have substan-

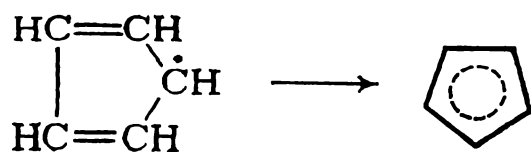
tially *non*-stoichiometric character [18, 19]. For example, the empirical formula NaCl always has the tendency to shift to the side of a certain prevalence of the sodium atoms in the lattice. Titanium oxide can almost never be described by the formula TiO; its composition varies, depending on the oxygen pressure in the environment, from $\text{TiO}_{1.25}$ to $\text{TiO}_{0.60}$. Zinc oxide always has an excess of zinc atoms which are arranged between the lattice knots, and the composition of zinc oxide is therefore often $\text{Zn}_{1.1}\text{O}$ or $\text{Zn}_{1.2}\text{O}$.

It is necessary to point out that there is still another difficulty with which the valency problem meets, and which has also been discovered by the modern means of physical study of crystals [13]. In some cases, a lattice is formed where atoms of the same elements are present in two different positions. For example, half of the thallium atoms in the crystal lattice of TlSe are arranged at the apices of a large octahedron, while the other half at the apices of a tetrahedron [15]. Chlorine atoms of some crystal modifications of CrCl_3 are also arranged in non-equivalent positions [12]. All these facts indicate that the bonds of atoms of one element can exist in different states. This phenomenon is still explained by the "classical" method: the lattice of TlSe is described by the "valency" formula $\text{Tl}^1 + \text{Tl}^3 + \text{Se}_2^{2+}$. But this formula only describes what is already known: thallium has two different bond states. It fails to describe the character of these bonds. It is evident that this "classical" explanation is quite inapplicable to the case with CrCl_3 where the atoms of chlorine are in different bond states.

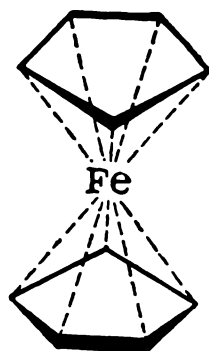
Bonds in Sandwich Compounds. A new class of organometallic compounds has recently been discovered. Because of the two-layer structure, they were given the name of sandwich compounds [20, 21]. Ferrocene, or dicyclopentadienyl iron, is the most studied one. It is obtained by the following reaction:



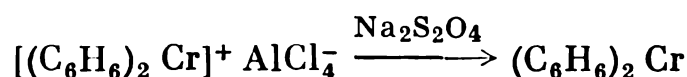
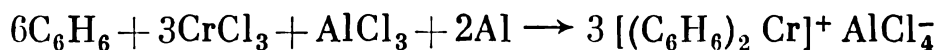
The studies of ferrocene have shown that its molecule has quite an intricate structure. Two pentadienyl rings lie in parallel planes at a distance of 0.332 nm from one another, while the atom of iron is located between them, at a distance of 0.166 nm from each ring, and 0.205 nm from each of the ten carbons. Each carbon atom in the pentadienyl rings becomes equal:



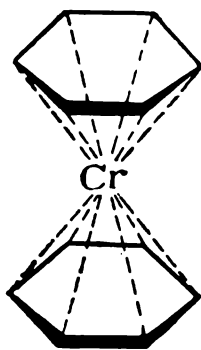
The molecule of ferrocene has thus the structure of a pentagonal antiprism with an iron atom in the centre:



The structure of dibenzene chromium, $(C_6H_6)_2Cr$, is even more interesting. This compound is obtained from benzene (whose structure has no unpaired electrons) and $CrCl_3$ in the presence of aluminium chloride and aluminium powder:

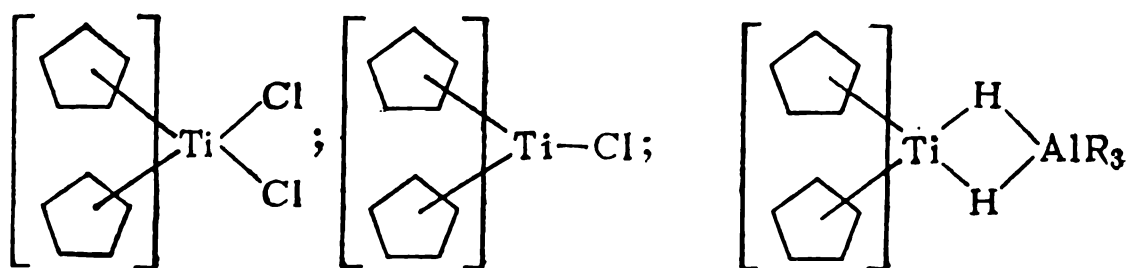


The X-ray studies of dibenzene chromium have shown that its molecule has the structure of a hexagonal antiprism with a chromium atom in the centre:

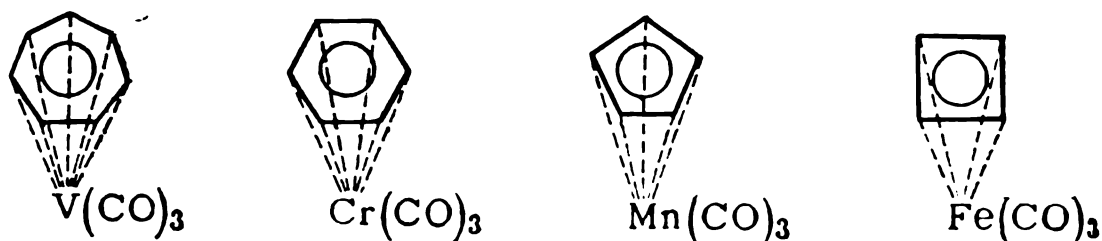


The distance between the chromium atom and each carbon is 0.219 nm, and the length of the carbon-carbon bonds in the benzene ring is 0.138 ± 0.005 nm (instead of 0.140 nm in free benzene).

Sandwich compounds with cyclopentadienyl ligands are quite numerous. Metallocenes of cobalt, nickel, titanium, and of other metals have been synthesized and studied. The following titanocenes are known for example [21]:



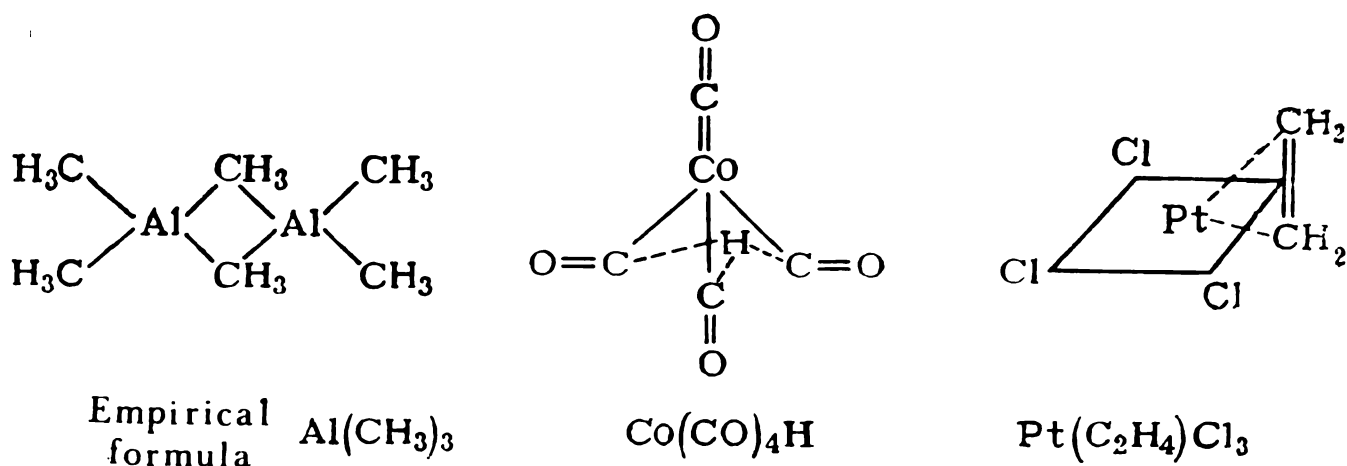
Semisandwich type compounds with tropylium, or cycloheptatrienyl, benzene, cyclopentadienyl, and cyclobutadiene have also been obtained [21]:



The character of chemical bonds in sandwich compounds was discussed from the quantum mechanical standpoints by many authors [for example, 16, 22]. But whatever the true character of the bonds may actually be, it is quite evident that this character is peculiar. The bonds in these compounds do not obey the classical laws. It would be senseless to assume the iron atoms in ferrocene and the chromium atoms in dibenzene chromium to be decavalent and dodecavalent, respectively.

Thus, the concept of chemical bonds different from classical intervenes not only in crystal chemistry but also in organic chemistry, where a molecule still remains the main chemical particle.

In his paper dedicated to the peculiar position of the valency problem in modern chemistry, Syrkin [16] gives many examples of existence of multicentre bonds in molecules:



These examples prove that there are no grounds for any calculations of the "number of bonds" by which the valency of an element in a compound can be established.

Chemical Bond from the Aspect of Quantum Mechanics and the Valency Problem. Our knowledge of an atom and a molecule has substantially changed with the development of quantum mechanics. A molecule is no longer regarded as a combination of atoms bonded by certain "affinity units", but as a complicate system of nuclei and electrons which move in agreement with the laws of quantum mechanics.

The calculation of the simplest molecules (H_2 and H_2^+) gave birth to quantum chemistry—the science studying the structure and properties of molecules by the methods of quantum mechanics.

At the present time electronic computers can calculate complicated molecules, various molecular complexes of polymers, and biological systems. The methods of quantum chemistry have also been improved in the course of 40 years. These methods are used to characterize the structure and properties of molecules from the quantum chemical aspects. But it should be noted that the main progress, made in quantum chemistry in the lapse of the past two decades, has only become possible with the development of computers and is therefore characterized as the progress in accumulation of quantitative information on the basis of concrete calculations. As to the development and extension of our qualitative concepts of chemical bond, they have remained substantially unchanged since 1940s. It is therefore quite up to date to examine the simplest two-electron molecule (H_2) by the Heitler-London method (valence bond method) and the molecular orbitals method (one-electron approximation).

Stable states of such a system (two electrons in the field of two similar nuclei) can only be explained by quantum-mechanical concepts and are connected with the following characteristics of the electron structure of the molecule in question:

(1) the minimum of full energy of the system at a certain internuclear distance;

(2) deformation of electron density in a molecule (compared with electron density of fully isolated atoms) consisting in a relative increase in electron density in the space between the nuclei.

The latter is the general characteristic of the covalent bonds. Such bonds are present not only in diatomic homonuclear molecules but also in molecules of organic compounds, weakly polar systems with sufficiently uniform distribution of electron density.

The distribution of electron density in a molecule in systems with ionic bonds could better be compared with electron density of the corresponding ions rather than of isolated atoms. But this comparison is seldom used because it has not given a quantitative criterion of the bond strength. The latter is determined by the depth of the minimum at the energy surface. In the case with a “purely covalent” model, said energy characteristics correlate with redistribution of electron density in the space between the nuclei. Such correlation is senseless in a “purely ionic” model. It should be understood that both models are very simplified. Chemical bonds in real systems are neither purely ionic nor purely covalent. The energy minimum and the character of distribution of electron density in a molecule account for its relative stability. It is difficult to predict what factors will be most important here.

Of course, any quantum-chemical method should be considered satisfactory provided it gives a satisfactory picture of distribution of electron density and the energy characteristics of a molecule. Using a certain quantum-chemical method we can often compare characteristics of chemical objects with some *quantum-chemical* characteristics.

Within the scope of the molecular orbitals method, such characteristics are one-electron energy levels and the corresponding coordinate wave functions (molecular orbitals). The classification of these characteristics according to the types of symmetry can often give quite an illustrative, although simplified, picture of the electron structure of a molecule. For example, the chemical bond in homonuclear diatomic molecules is, in accordance with these concepts, associated with the prevalence of the filled bonding orbitals over antibonding ones.

The Heitler-London method describes the chemical bond in a different way: each atom has a certain number of unpaired (valency) electrons; as a chemical bond is formed, the valency electrons of two atoms combine in pairs with antiparallel spins. Here the formation of chemical bonds resembles the pre-quantum views on the combination of atoms as a result of "saturation of valency". An important place in such a description is occupied by the concept of spin-valency of an isolated atom (i.e. the number of valency electrons).

One might understand that quantum mechanics has solved the problem of valency by identifying it with spin-valency and by finding its application within the frames of the valence bond method. But it would be expedient to stipulate the following:

(1) The Heitler-London system can only be applied to the *simplest* version of the valence bond method, and cannot always give qualitative characteristic. The number of cases where this approximation does not hold is much greater. The value of such an illustrative description of the chemical bond is therefore quite disputable.

(2) The valence bond method is at the present time almost fully displaced by the molecular orbitals method, while the latter fails to give any quantum-chemical characteristics which could agree with the classical concept of the atom valency.

(3) The concept of spin-valency refers to an isolated atom and, to a certain degree, determines its properties. But if we consider valency as a characteristic of atoms in a molecule, we shall not find a quantum-chemical analogue to it.

Now a question arises, as to what contribution quantum mechanics made into chemistry. It has substituted some concepts for others, which are undoubtedly more perfect, but what is especially important, these concepts are different from the former ones. The new concepts helped very much explain the chemical structure and chemical properties of matter. High coordination numbers of "low-valency ele-

ments", the existence of the multicentre bonds and the formation of sandwich compounds can be explained from the standpoints of quantum chemistry. This fact alone differs it from the classical chemistry. Even more extraordinary (with respect to the classical concepts) is the principle of qualitative indiscernability of strong and weak interactions inside a molecule, i.e. what the classical chemistry would call chemical bond proper, and what is named the mutual effect of atoms which are not connected directly. According to this principle, single two-centred bonds, as a criterion of measure of valency, can be absent in a molecule at all. In his textbook "Inorganic Chemistry" [23] Shchukarev discusses the structure of N_2 , CO, and BF molecules to illustrate contradictions between the quantum mechanical and classical concepts which lead to unexplainable paradoxes. He attracted our attention to the "ambiguous position of the valency theory" and to the amorphousness of the very concept of valency.

Many chemical problems, and in the first instance the problems of reactivity of micro-objects, are to be solved. Quantum chemistry meets here with significant computation difficulties, and in many cases chemists still continue using pre-quantum concepts in their attempts to solve problems where quantum mechanics proves practically inapplicable.

From what we have said becomes clear the importance of uniting the chemical concepts with the concepts of quantum mechanics without substituting one concept for another, but trying to find agreement between them.

To what extent this can be done with respect to the valency problem will be the subject of our discussion in Chapter 7.

To summarize, the physical methods of studying the structure of substances, the discovery of "non-classical" sandwich compounds, and advances made in the application of quantum mechanics to chemical objects have produced significant, and even radical (as far as most inorganic compounds are concerned) changes in our views on the chemical bond [23-27]. In this connection the "number of bonds formed by a given element", which was formerly used as the general criterion of valency, proved to be absolutely useless in chemistry. Calculation of this "number" from empirical formulas can only mislead us in our assessment of the actual reactivity of an atom. But using the same considerations we can admit that the concept of valency itself is now in an ambiguous position: it has lost its former criteria, and gained nothing to substitute for them.

Before we proceed now to discuss the future of this concept, it is necessary to solve a radical problem of the relationships between the concepts of valency and chemical bond. It is the solution of this problem that will help us decide whether or not we need the concept of valency at all and if we need it, then what this concept implies by

side with the concept of chemical bond. There is *only one way* to solve the problem, the historico-chemical way, by which we can study the evolution of these two concepts and their mutual interdependence at all stages of the history of chemistry.

This is the main problem which we shall try to solve in this book.

2. Valency: Is It the Property of a Free or a Bound Atom?

As a scientific concept develops, it deeper discloses its object. But the development of a concept, or in other words, its evolution never means the change or replacement of its original subject. Otherwise it would mean replacement of one concept by another, of this other concept by some third one, etc., rather than the development of the original concept. Evolution of a concept means both preservation and modification. This is the accumulation of information and the pass-over from one level of knowledge of the subject to another without changing the term denoting the concept and with preservation of certain invariant contents of this concept.

Schematically the evolution of a concept can be represented as shown in Fig. 1*a*. The invariant contents are as important as the changing component—the accumulating information which also passes into the invariant as soon as a new level is attained.

Rare cases where the invariant proper changes indicate either the full renunciation of the original sense of the concept, and hence the renunciation of the concept itself*, or the change of the object of the concept, for example, introduction of other fragments of material reality into the original object**. In the latter case the term may persist, and even retain part of its former content, but the continuity of the invariant will inevitably be broken and logical discrepancies interfere with the evolution of the concept, which is shown schematically in Fig. 1*b*. This short digression to logics was expedient before we turn to discuss the evolution of the concept of valency.

The concept of valency, invented in the science originally to describe the properties of a certain object, was later used to characterize the properties of quite a different object. In other words, the evolution of the concept of valency is just that rare case where the invariant of the concept itself changes.

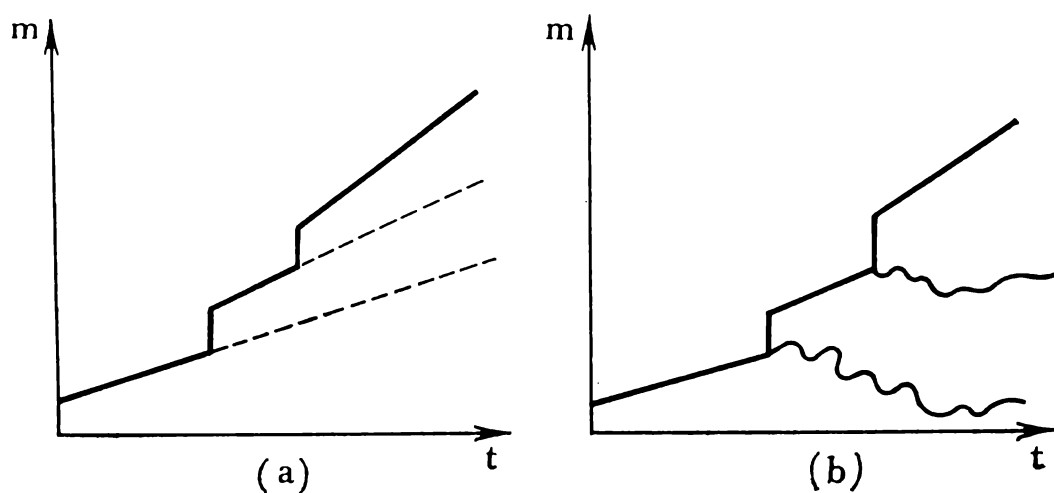
* For example, Butlerov, to explain inequality of chemical bonds in a molecule, first used the concept of “different units of affinity” (1861) [28, p. 86], but later (1863) he came to a conclusion that his earlier hypothesis had been untenable. He gave up his former concept and introduced a new one instead, the mutual effects of atoms [28, p. 112].

** The development of the valency concept is such a case. See below.

The history of formation and development of the concept of valency will be discussed in more detail in Chapter 2. Here we shall only point out (with allusion to Chapter 2) that the concept of valency in the works by Frankland and Kekulé was originally used to describe the "combining power" or the number of units of affinity of a chemical element inherent in it before it becomes a part of a chemical compound. This original concept underwent modification and was later used to designate not the number of free affinity units inherent in an isolated atom, but a state of an atom combined in a molecule. In other words, the concept of valency as the cause of chemical bond (Butlerov) was thus identified with the chemical bond itself (Chugaev, Menshutkin).

Of course it is wrong to put together the cause and the effect, but this is a historical fact and can be explained by certain reasons. Even today the opinion exists that as a chemical element passes from one compound to another, as well as from a "simple body" into a compound, it remains invariable. For example, carbon remains carbon in diamond, in methane, in benzene, and in acetic acid. And although we know now that in all these cases (above named compounds) it is not the atom of carbon but only its nucleus and electrons (i.e. entirely new structural units) that are preserved, no one will dare call it some name other than carbon. At least we, the authors of this book, shall not dare. We should rather remind the reader that there are two definitions of a chemical element: (1) "Chemical elements: a combination of atoms characterized by the same charge on their nuclei" [29] and (2) "Chemical elements: component parts of matter built up of atoms characterized by the same charge on the nucleus and by the same electron shells" [30]. But only one of them can be considered adequate. We should like to remind also that it is wrong to identify Cl' with Cl^- , $2\text{O}''$ with O_2 , H with proton,

Fig. 1. Graphic presentation of the evolution of the valency concept with continuous (a) and ruptured (b) invariant line (m is information and t is time).



and $n\text{Na}$ with $n\text{Na}^+$, etc. Yet, some do it; and they adhere to the first definition of the element.

What is most important here is that, because of this illogical identification, the valency concept is almost automatically transferred onto another object, as if the difference between bound and free atoms has not long been established. We beg the reader to pardon us for our second reference to the same "Course in Chemistry" [2], but it will help us illustrate these logical discrepancies. The textbook reads: "Valency is the property of an atom of one element to combine with one or several atoms of another element."

From this definition it follows that valency is the property of free and only free atoms, since a bound atom either cannot combine with some other atoms at all, or, if it can, the number of atoms with which it can combine cannot be regarded as the valency number.

A little further, on the same page, the textbook reads: "...titanium forms the following compounds with chlorine: TiCl_2 , TiCl_3 , and TiCl_4 , in which (i.e. in these compounds, V. K.) the valency of titanium is $+2$, $+3$, and $+4$ " [2]. It follows from this explanation of the definition that valency is not the property of a free atom but that of an element bound in a compound. We are not inclined to sophisms at all: the cause can clearly be found in the effect, but one may not identify the cause with the effect. Unfortunately they are identified in this case, though, perhaps, the authors did not intend to.

So, as the theory of valency was in its progress, the question naturally arose: what in fact is valency, the property of a free or of a bound atom?

Only one monograph, that of Tatevskii [28], gives a direct answer to this question. The monograph has a special section "The Concept of Valency in Classical Theory and in the Theory of Spin-Valency" (p. 36). The answer is formulated as this: "The classical theory of chemical structure contained a concept of a certain number (valency number) which was understood to be constant for an atom of an element in a certain series of its compounds. This concept of valency was used in a certain measure to characterize the state of an atom in a molecule, rather than in an isolated state (not bound in a certain molecule).... As far as the valency of an atom in an isolated state is concerned, it seemed meaningless in the classical theory of chemical structure (the valency of a free atom in the classical theory is zero).... The picture is different in the spin-valency theory: the valency number is referred here to an atom in the free state (as a number of electrons with unpaired spins), while the valency number of an atom bound in a molecule is defined by the spin-valency theory in one possible way: it should be assumed to be equal to the valency number of an isolated atom.... It follows that the spin-valency theory did not develop the classical theory of chemical structure but unno-

ticeably substituted new postulates for them which contradicted the concepts of the classical theory" [28, p. 37-39].

According to Tatevskii, the concept of valency can therefore be considered only in the theory of chemical structure, and only as the reflection of properties of an atom combined in a molecule, while the concept of valency as a property of an isolated atom seems to him to be alien to classical chemistry. It can only exist in the theory of spin-valency whose "untenability" became the subject of a special section in his book [28, p. 46].

Like the whole of Tatevskii's book, these speculations are interesting in the sense that they concern the most important, in a way, methodological problems of the relationships between the classical and quantum-chemical theories. But is Tatevskii right in his flatly formulated statements? The answer shall be found in the history of the theory of valency which will be the subject of the second and subsequent chapters.

3. What Are the Objects of the Theory of Valency?

The role and the objects of the valency theory seem to be entirely dependent on, and even derived from the answer to the previous question, namely, what we mean by valency? But these two problems are closely connected and the analysis of this connection from the historical and chemical aspects gives us a simple answer, what the term valency implies and what is added to it by the working success of the theory.

In this book we shall therefore not only discuss *what* the object of the theory of valency *should be*, but rather consider the theories themselves, both the theories of the past and present, we shall analyse the problems which these theories have already solved and shall thus reveal the functional efficiency of the valency concept as the tool of scientific study in each of these theories.

Advantages, that we shall take of it, will be evident from the further discussion, while here we shall only give a general classification of all ideas and theories which could in this or that way be attributed to the theory of valency. Acquaintance with the history of the theory of valency shows that chemistry has known at least three trends in the scientific investigations, each of the three being characterized by its own specific attitude to the concept of valency, and hence by its own efficiency of using this concept.

The first trend. These are the theories of valency proper [31-33]. They comprise the theory of Kekulé; ideas of Delavaud; the theories of partial (residual) valencies of Armstrong, Pickering, Thiele, and others; ideas of van't Hoff, Werner; the theories of Abegg and Stark;

the theory of spin-valency. All these theories use the concept of valency as one without which it is impossible to understand chemism. And since chemism begins where two or more isolated atoms interact to form an aggregation, characterized by the minimum of the full energy at certain internuclear distances, or, as some put it, "descending into the energy well", all these theories regard valency as a measure of reactivity of a free atom of a chemical element, i.e. that they give us a criterion by which we can assess the possibilities of an atom of a given element, viz., what bonds this atom can form with the atoms of the same and other elements.

The second trend. These are "valency theories" as well, but of a different kind. They are discussed in the book "Valence" by Coulson [26] or, for example, in "Valence Theory" by Murrell, Kettle, and Tedder [34]. These books regard all theoretical chemistry as the theory of valency. Thus Coulson regards the theory of atom structure, the "molecular orbitals method", the "valence bond method", the theory of hybridization, of bond conjugation, the theory of ligand field, the theory of chemical bond in solid substances, and the theory of the hydrogen bond, as only fragments of the valency theory. Murrell, Kettle, and Tedder, whose intention was to fill the blank spaces in the semiquantitative picture given by Coulson in his book, discussed the same problems in their theory of valency [34] but added also the theory of chemical reactions, the elements of the theory of transition state in particular. Thus, the theory of valency turned to cover all problems connected with chemism: potential chemical reactivity of atoms, causes of aggregation of atoms into molecules, description of all possible types of chemical bonds in molecules and other particles of chemical compounds, and finally, the mechanism of reactions as redistribution of bond electrons in the transition state.

Is it rightful to widen the theory of valency to such an extent?

The third trend. The followers of the third trend use the concept of valency in a special way. They do not regard the valency theory, but discuss various sections of chemistry where the necessity arises to characterize the properties of a bound atom. The necessity does exist, since in structural chemistry it is impossible to characterize chemical bond without describing the properties of the interacting components. The properties of bound atoms (to be more exact, nuclei) are therefore characterized by some other concepts, such as coordination number, oxidation number, or the degree of oxidation, effective charge, free valency index, and ... simply valency. The valency number is usually derived from the empirical formula of a compound whose composition is assumed to be ideal, i.e. the quantitative relationship between x and y in a compound A_xB_y is regarded as a simple integral multiple: AB , AB_2 , A_2B_3 , etc. The method is only approximate, and we have already criticized it.

But whether it should or should not be used, is a question difficult to decide. In many compounds in the condensed state, mostly in solid substances, atoms of one element often have different properties, which is usually explained by the presence of atoms of a given element in various valency states. For example, in chlorides, oxides, and sulphides of mercury, cadmium, thallium, chromium, and many other metals, the atoms of these metals are found in different valency states: Hg^{I} and Hg^{II} , Cd^{I} and Cd^{II} , Tl^{I} and Tl^{II} , Cr^{II} and Cr^{III} . The different properties account for the different functions of compounds in chemical processes. For example, it is indicated that the number of active catalytic centres in metal oxides depends on the ratio of the valency numbers of metal atoms.

It is probably unnecessary to emphasize the importance of information related to such differentiation of atoms in the composition of chemical particles. But as to rightfulness of using the valency concept for this differentiation, it should be discussed in that form in which the problem was presented in the previous section of this chapter. If the concept of valency persists in chemistry to characterize the state of bound atoms, it should at least be separated from the other concept, also known as valency, and used to characterize potential power of an atom to combine with other atoms.

Thus we have named the three trends in the investigations dealing with "valency". In one of them valency is not only a concrete and working concept, but also a developing one, the scope of which is widened and enriched as the science is progressing. In the other trend this is something general, which must be synonymous to chemistry. In the third trend (like in the first) this is a concrete concept, and working too, but perhaps more formal and not accounting for the actual number of chemical bonds or the true composition of the crystal lattice. But this concept works, and therefore its formalism is perhaps only apparent.

In subsequent chapters we shall try to clear out in more detail the role which the valency concept plays in various chemical theories.

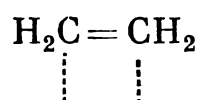
4. Can Valency Be Characterized by Numbers Other Than Whole?

This section is dedicated to a very delicate problem. The point is that, whatever the chemists understood by valency, the property of a free or bound atom, they always used only whole numbers to describe it. This was explained by several factors. In classical chemistry, in accordance with the laws of stoichiometry and the concept of atomic discreteness, valency is expressed by the whole number of affinity units. All electronic theories, in accordance with the concept of structure of valency shells of atoms, express valency by the whole

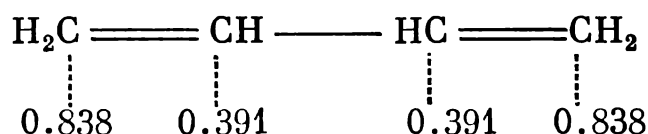
number of electrons or vacant spaces in the electron shells*. For this reason, whenever we say that the atom of a given element has the valency n , the n is always a whole number from 1 to 8. When the atom is bound in a molecule the considerations are the same. The history of chemistry does not know cases where a free or a bound atom was characterized by a fractional number of valency, e.g. 1.5 or 2.3, etc.

And yet fractional valency does appear, both in classical and quantum chemistry. And the necessity of fractional units arises only when an atom enters a molecule. And here it is necessary to pay attention to the delicacy of the problem which we have mentioned earlier. At first sight one might understand that the valency concept here refers only to bound atoms, but it is not actually so.

The first ideas that valency could be expressed in numbers other than whole appeared in the second half of the past century (see Chapters 2 and 4), and it was understood as incomplete utilization of affinity units. Thiele, for example, called it "partial valence" [35]:



These concepts were used in the same sense in quantum chemistry, which sometimes alluded to "free valency indices" or simply "free valencies" which were expressed by fractional numbers (from 0.1 to 0.8) [26]:



In both cases valency is expressed by fractions of a unit, i.e. only parts of "affinity units" which, according to Butlerov, characterize potentialities of a free atom.

It would be expedient here to remember how Butlerov in his first paper "On the Chemical Structure of Substances" explained incompletely utilized affinity of atoms, or "elementary shares" that became part of a molecule. "Each elementary share is characterized by a certain pre-existing amount of force which produces chemical phenomena (affinities). Part of this force or its whole amount is consumed (bound, converted into another form) during a chemical conversion" [27, p. 71]. And although Butlerov mentions here incompletely utilized whole affinity units (e.g. C^{IV} gives $\text{C}^{\text{II}}\text{O}_2$ and $\text{C}^{\text{IV}}\text{O}_2$) and not fractional units, he emphasizes the importance of atomicity, i.e. valency as the *pre-existing* amount of force that produces chemical phenomena. And if part of affinity of atoms combined in a molecule has "remained free, the body can combine directly with various par-

* For more detail see Chapter 9.

ticles, and the cause of this ability of the body depends on the element whose affinity has not been utilized completely during formation of the complicate body”.

The idea of partial valency was developed by Thiele in the same spirit, except that his incompletely utilized or residual valency was described by fractional numbers, whose values were less than unity. “Atoms tend to form as many bonds as possible”, says Syrkin [17, p. 905]. But in reality they do not always form all bonds that they can. Part of their structural abilities remains unused and this can be regarded as residual valency responsible for the activity of saturated molecules, e.g. their ability to form complexes, low-energy active complexes in particular.

What is the extent to which these abilities can be utilized, and on what does it depend? The answer to these questions can only be found alongside with the theoretical explanation of a great variety of the energy characteristics of interatomic bonds.

5. Valency and Atom Reactivity

We have come now to the problem whose solution is connected with an entirely new approach to the evaluation of the theory of valency. We mean that stage of the development of the theory at which the concept of valency, spin-valency included, becomes a special case of a wider, and deeper in sense, concept of the atom reactivity.

The difficulties that we now associate with the concept of valency are in many respects the result of the fact that this stage of development of the theory has probably been attained. The intense development of this theory, characterized by the extension of the classical concept of valency as potential abilities of a free atom, to new branches of chemistry, and by adaptation of this concept to new discoveries, has been actually exhausted. The theory of spin-valency, which at the present time is the latest development in this way, has explained the physical essence of the discrete, and quite definite numerical value of valency. But now, as it was shown in the first section of this chapter, the discovery of new types of chemical compounds and new data on the actually existing chemical bonds in crystals, complexes, as well as in molecules, requires urgent theoretical studies to give an entirely new picture of the structure of chemical particles. It has become evident now that atoms not only tend to form as many bonds as possible, but they do form them wherever possible, and this explains the multitude of complex compounds, whose existence was not suspected of till recently. And here the question arises: by what valency means do atoms form such a variety of bonds, still leaving incompletely utilized valencies? And along with this another question arises concerning the simplest molecules: why are strong bonds formed in cases where weak bonds might be

expected? On what does the difference in the energy of bonds depend, for example in these molecules (kcal/mole):

K—K	11.8	Cu—Cu	46.5	F—F	37.6
Rb—Rb	10.5	Ag—Ag	37.5	Cl—Cl	58.0
Cs—Cs	10.3	Au—Au	50.0	Br—Br	45.4

The answer to these questions can undoubtedly be found in the possibilities of atomic structures which are not yet sufficiently studied. But the theory of spin-valency, with its central concept of valency as a whole-number characteristic of valency potentialities of atoms, does not answer these questions. And this circumstance is disadvantageous to the progressive (on the whole) concepts of spin-valency, and also to the concept of valency in general.

The question of intense development of the valency theory becomes therefore very important [16, 26]. This development must be a substantial modernization of the spin-valency concept or a pass-over to an entirely new concept, e.g. such as the reactivity of an atom. The latter should probably imply (alongside with spin-valency) some other potentialities of a free atom with respect to chemical aggregation. There are some indications in the literature that such potentialities exist [e.g. 17 and 23].

A new field of theory is now being formed to describe the reactivity of an atom, otherwise known as the fundamentals of the theory of atom [34]. It is however based on the quantum theory of the Periodic system of atoms*, which is not interesting to the chemist except for one thing: only this theory can be used to better study atoms as pre-chemical systems, as a construction material for chemical particles. The new stage in the valency theory as a theory of reactivity of atoms is therefore connected with the advances in the development of the theory of chemical bond, and the theory of Periodic system.

References

1. *Concise Chemical Encyclopedia*, vol. 1, Sovetskaya Entsiklopedia, Moscow, 1961, p. 510 (in Russian).
2. *Course in Chemistry*, 2nd ed., revised, edited by Dmitriev, G. A., Luchinskii, G. P., Semishin, V. I., Part I, Vysshaya Shkola, Moscow, 1971, p. 93 (in Russian).
3. Chichibabin, A. E., *Basic Principles of Organic Chemistry*, 5th ed., revised and enlarged, ed. by Prof. Sergeev, P. G., vol. I, Goskhimizdat, Moscow-Leningrad, 1953, p. 49 (in Russian).
4. Menshutkin, B. N., *Course in General Chemistry (inorganic)*, 4th ed., revised, Goskhimtekhnizdat, Leningrad, 1933, p. 57 (in Russian).

* For the differences between the theory of Periodic system of atoms and the theory of Periodic system of elements see [36].

5. Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, N.-Y.-London-Sydney, 1962.
6. XVIIth International Congress of Pure and Applied Chemistry, Munich, 30 Aug-6 Sept. 1959, London, 1960.
7. Spitsyn, V. I., *Heptavalent state of neptunium and plutonium and the valency problem of actinides*, in book "Centenary of Periodic Law of Elements", Nauka, Moscow, 1969, p. 225-243 (in Russian).
8. Figgis, B. N. and Lewis, J., *The Magnetochemistry of Complex Compounds*, in book "Modern Coordination Chemistry", Interscience Publishers inc., N.-Y.-London, 1960, p. 400-454.
9. Semenov, N. N., *Some Problems of Chemical Kinetics and Reactivity*, 2nd ed., revised, Academy of Sciences Press, Moscow, 1958, p. 26-41 (in Russian).
10. *Hydrogen Bond, Collected Papers*, ed. by Sokolov, N. D. and Chulanovsky, V. M., Nauka, Moscow, 1964 (in Russian).
11. Boki, G. B., Belov, N. V., *Crystal Chemistry*, Great Soviet Encyclopedia, 2nd ed., vol. 23, Moscow, 1953, p. 419 (in Russian).
12. *Physical Methods in Advanced Inorganic Chemistry*, ed. by H. A. O. Hill and D. Day, Interscience Publishers, 1968.
13. Ormont, B. F., *Introduction to Physical Chemistry and Crystal Chemistry of Semiconductors*, 2nd ed., rev. and enl., Vysshaya shkola, Moscow, 1973 (in Russian).
14. Barnard, A. K., *Theoretical Basis of Inorganic Chemistry*, McGraw-Hill, N.-Y.-London-Toronto, 1965.
15. *Chemistry of the Solid State*, ed. by W. E. Garner, Butterworths Sc. Publications, London, 1955.
16. Syrkin, Ya. K., *Advances in Chemistry*, vol. 28, issue 8, 1959, p. 903-920 (in Russian).
17. Wong, C., Shoemaker, V., *J. phys. Chem.*, vol. 61, 1957, p. 358.
18. *Non-Stoichiometric Compounds*, ed. by Mandelcorn, Academic Press, N.-Y.-London, 1964.
19. Hannay, N. B., *Solid-State Chemistry*, inc. Englewood Cliffs, New Jersey, 1967.
20. Nesmeyanov, A. N., Perevalova, E. G., *Advances in Chemistry*, vol. 27, issue 1, 1958, p. 3-56 (in Russian).
21. Pauson, P. L., *Organometallic Chemistry*, Edward Arnold Publishers, LTD, London, 1967.
22. Dyatkina, M. E., *Advances in Chemistry*, vol. 27, issue 1, 1958, p. 57-73 (in Russian).
23. Shchukarev, S. A., *Inorganic Chemistry*, vol. 1, Vysshaya shkola, Moscow, 1970, p. 117 (in Russian).
24. Charkin, O. P., *Zh. vses. khim. ob. im. Mendeleeva*, vol. 17, No. 3, 1972, p. 251-258 (in Russian).
25. Volkenshtein, M. V., *Structure and Physical Properties of Molecules*, Acad. Sci. Press, Moscow-Leningrad, 1955 (in Russian).
26. Coulson, C. A., *Valence*, Oxford Univ. Press, 1961.
27. Tatevskii, V. M., *Quantum Mechanics and Theory of Molecular Structure*, Moscow Univ. Press, 1965 (in Russian).
28. Butlerov, A. M., *Collected Works*, vol. 1, Acad. Sci. Press, Moscow, 1953 (in Russian).
29. *Great Soviet Encyclopedia*, 2nd ed., vol. 48, 1957, p. 654 (in Russian).
30. *Concise Chemical Encyclopedia*, vol. 5, Sovetskaya Entsiklopedia, Moscow, 1957, p. 994 (in Russian).
31. Bykov, G. V., *History of Classical Theory of Chemical Structure*, Ch. 1, Acad. Sci. Press, Moscow, 1960 (in Russian).

32. Kuznetsov, V. I., *Evolution of Concepts of Basic Chemical Laws*, Nauka, Moscow, 1967 (in Russian).
33. Soloviev, Yu. I., *Evolution of Basic Theoretical Problems*, Nauka, Moscow, 1971 (in Russian).
34. Murrell, J. N., Kettle, S. F. A., Tedder, J. M., *Valence Theory*, London-N.-Y.-Sydney, 1965.
35. Thiele, J., *Lieb. Ann.*, 1899, Bd. 306, S. 87-142; 1901, Bd. 319, S. 129-143.
36. Trifonov, D. N., *Periodic System of Atoms*, in book "On Systematics of Particles", Atomizdat, 1969, p. 9-42 (in Russian).

Chapter **The Evolution** *Two* **of the Theory of Valency**

The roots of the valency concept can be traced in the atomistic theory of Dalton who synthesized the empirical concept of simple multiplicity with theoretical concepts of the atomic structure of individual substances. Precursors of the valency concept can also be found in some Avogadro's works published in 1814-1821. Avogadro was the first to equate two atoms of a halogen with one atom of oxygen or sulphur. He established equivalency of atoms of phosphorus, arsenic, and antimony from chemical formulas of their halides and oxides. In the same way he established the analogy between carbon, silicon, titanium, zirconium, and tin long before it became a commonplace. But all these ideas were used in the development of the theory of valency much later.

The intense work done by Berzelius in the analysis of chemical compounds and determination of their correct chemical formulas promoted the foundation, in 1826, of the system of chemical symbols which was very much like that we use now. But Berzelius did not arrive at the concept of valency. True, he formulated some general rules of "combination of atoms" which were rather arithmetical in character. For example, he established the "series of sulphur" and the "series of nitrogen". Compounds belonging to the former series were designated RO_n and to the latter R_2O_n . But the rule was only too general. It embraced all elements and suggested that each series comprises a great many of members (n being 1, 2, 3...); this indefinite continuity made the system inoperative.

It is also necessary to mention the difficulties which were met by the rules of combination of atoms in the study of organic compounds. The development of the structural concepts was just started and they could not explain the nature of organic substances. But the complexity of their atomic composition was a clear obstacle to Berzelius and his contemporaries in their attempt to formulate laws by which the atoms are combined into particles of a chemical compound. The regularities of the atomic composition of inorganic and organic compounds were then unknown, and formulas of organic compounds were over-complicated by Berzelius who ascribed dualism to their structure.

The unitary system by Gerhardt was a marked step towards a more adequate interpretation of the atomic composition, and towards direct precursors of the theory of valency. The main postulate of the unitary theory suggested integrity of a molecule of any chemical individuum. This theoretical proposition could not but stimulate revision of the former dualistic views on the composition of particles of chemical compounds. This meant the return to empirical formulas, but these formulas now corresponded to the atomic composition of molecules. After establishing such formulas, Gerhardt and Laurant strictly differentiated between the equivalency of the atoms of the halogens among themselves and the equivalency of oxygen, sulphur, selenium, and tellurium; they also established that an atom of each element standing in the oxygen group is equivalent to two atoms of hydrogen or two atoms of any of the halogens. Connections between regularities by which atoms combine into molecules of inorganic and organic compounds were later established. The theory of types proposed by Gerhardt, and developed later by Williamson, Odling, Wurtz, Kekulé, and others, helped explain these connections and understand the true sense of valency. In 1846, Laurant used correct empirical formulas (derived by Gerhardt for ethyl alcohol and ethyl ether) to suggest that these compounds were the products of substitution of water (HHO), like potassium hydroxide and potassium oxide [1]. In 1850, Williamson confirmed this idea experimentally. He proved equivalency of radicals C_2H_5 , CH_3 , C_2H_3O , and others to one hydrogen atom, i.e. he established the connection between equivalency of atoms and radicals. Later, in 1851-1852, Williamson and Gerhardt arrived at the idea of multiatomic radicals equivalent to two or three hydrogens, and the idea of doubled types [2].

As William Odling, a friend and disciple of Williamson, was expressing oxides and hydroxides of metals by typical formulas, he came to the idea (1854) of "multi-atomic" elements. And he used superscript dashes to express atomicity, e.g. H' , O'' , K' , Sn'' , Bi''' , Fe''' , etc. [2, 3].

1. Formation of the Concept and Theory of Valency

Early ideas that elements could be differentiated by valency, or atomicity, can be found in the works by Gerhardt, Laurant, and especially Williamson and Odling. Nevertheless, the concept of atomicity is usually associated with the name of Frankland. The problem of priority will be discussed later. In this paragraph we only want to show the process of formation of the valency concept.

The English scientist Frankland, the adherent of Kolbe's theory of paired radicals, studied the properties of organometallic compounds

and in 1852 came to a conclusion that it was necessary to revise the theory of radicals in general and to accept some postulates of the theory of types. He extended the ideas of Laurant, Williamson, Gerhardt, Odling, and others, concerning the relationships between the equivalency of radicals and the equivalency of atoms, to organometallic compounds, and proposed the concept of "combining power" of atoms.

According to the "paired" theory of Kolbe (1850), which is a further development of Berzelius' dualism, and organic compound contains a radical with two equivalents of carbon C_2 , the equivalent mass of carbon being $E_C = 6$. According to this theory, only C_2 or an equivalent of metal in organometallic compounds is the point which is attacked by affinities of other elements (oxygen, chlorine, etc.). According to Kolbe, saturability of C_2 or a metal equivalent does not depend on whether or not they are connected with other organic radicals. Thus Kolbe's theory defended the old, pre-Gerhardt views, according to which a molecule of an organic compound was composed of radicals capable of independent existence. According to this theory, a molecule of an organometallic compound must also consist of radicals and atoms of metals as independently existing particles.

Frankland's experiments showed however that the oxidability of organometallic compounds differs from that of pure metals. For example, ethyl tin does not form two but only one oxide, $(C_4H_5)SnO$, diethyl zinc $(C_4H_5)Zn$ does not give oxides at all, etc.*. From his own observations, and also from the ideas of Wurtz and Hofmann (concerning amines as products of ammonia substitution) and of Williamson (concerning alcohols and ethers as products of substitution of water), Frankland came to a conclusion that organometallic compounds are derivatives of inorganic types obtained by substitution. The types meant by Frankland were metal oxides (MeO , MeO_2 , MeO_3 , MeO_5), in which the radicals were substituted for one equivalent of oxygen [4, 5]. And here Frankland made a very interesting conclusion on the composition of some binary inorganic compounds: "When the formulae of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction; the compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of the elements to form compounds containing 3 or 5 equivalents of other elements, and it is in these proportions that their affinities are best satisfied; thus in the ternary group we have NO_3 , NH_3 , NI_3 , NS_3 , PO_3 , PH_3 , PCl_3 , SbO_3 , SbH_3 , $SbCl_3$, AsO_3 , AsH_3 , $AsCl_3$, etc.; and in the 5-atom group NO_5 , NH_4O , NH_4I , PO_5 , PH_4I , etc. Without offering any hypothesis regarding the cause of this symmetrical

* Frankland uses equivalents in his formulas. The equivalent of carbon is 6, of oxygen 8, and equivalents of metals correspond to halves of their atomic masses. Correct formulas of the given compounds are $(C_2H_5)_2SnO$ and $(C_2H_5)_2Zn$.

grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, *the combining power of the attracting elements*, if I may be allowed the term, *is always satisfied by the same number of these atoms, irrespective of their chemical character*" (italicized by *M. F.*) [5, p. 368].

This quotation is often used to prove Frankland's priority in the development of the theory of valency. But using equivalents and the corresponding formulas, Frankland arrives at a wrong conclusion that the elements given in his examples (N, P, As, Sb) satisfy their affinities by the same number of the uniting atoms "irrespective of their chemical character"* (i.e. that hydrogen, chlorine, and oxygen are characterized by the same valency). This quotation shows that Frankland established only a partial regularity. He did not extend his "combining power" of the nitrogen atom onto other elements, but only applied it to those elements (tin, antimony, arsenic, zinc, mercury) whose organometallic compounds he investigated as derivatives of the corresponding oxides. From Frankland's type formulas based on equivalents ($E_C = 6$, $E_O = 8$), it followed that one element could have different "combining power".

So it is hardly rightful to ascribe the formation of the valency concept to Frankland, or to contend that he approached this concept closer than his predecessors. His merit was that he proved the ideas by Laurant, Williamson, and Odling concerning equivalency of radicals and atoms, using organometallic compounds as examples. Thus he arrived at a certain "combining power" inherent in the atoms of elements which was responsible for the formation of compounds. But, as Russel puts it, "Frankland's use of incorrect atomic weights (i.e. equivalents,— *M. F.*) prevented him (at that time) from being able to arrive at correct values for the valencies" [6, p. 110]. He was not even able to determine the unit of valency.

Frankland's idea of the combining power occupies a very important place in his large work on organometallic compounds (1852). He did not further develop his ideas till 1858, for probably he did not attach great scientific importance to them. Maybe it was because of the negative attitude to his "combining power" in Kolbe's textbook (1854).

Although in his work on organometallic compounds Frankland deviated from some propositions of the theory of radicals, in the eyes of organic chemists he still supported the electrochemical dualism and the system of equivalents, and for these reasons his ideas could not produce the appropriate influence. And after all,

* In his book "The History of Valency" [6] Russel cites Frankland but, for unknown reasons omits the ending of the sentence, "irrespective of their chemical character".

the theory of types by Gerhardt, which was formed in 1852, might have overshadowed Frankland's ideas. In our opinion, these facts can explain why Frankland's ideas did not stimulate any new generalization in this field before 1857-1858.

The working theory of valency could have been formed only after derivation of correct empirical formulas for organic and inorganic compounds, after the concepts of atom, molecule, and equivalent were differentiated.

The decisive role in the formation of the theory of valency belongs to Kekulé [2, 3]. He was probably influenced by the works of Williamson, Odling, and Frankland. This influence might be the result of his direct contact with Williamson and Odling during Kekulé's stay in London from 1853 till 1856. There were no direct contacts between Kekulé and Frankland.

In 1854, while developing the method of preparing thioacetic acid, Kekulé came to important conclusions which supported the system of atomic weights proposed by Gerhardt and disproved Frankland's conclusions concerning the equivalence of atoms of chlorine and oxygen [3]. Williamson's and Odling's works, and perhaps especially Wurtz' work*, which laid a straight way to understanding valency, were the stimuli that drove Kekulé to his conclusions. In his paper, published in 1857 [7], Kekulé explains the theoretical sense of the three types proposed by Gerhardt (H_2 , H_2O , and NH_3). He writes: "The number of atoms of one element that combines with one atom of another element depends on basicity or relationship-size (*Verwandschaftsgrösse*) of the component parts. The elements fall into three main groups in this respect:

- (1) monobasic, or monatomic (I), e.g., H, Cl, Br, K;
- (2) dibasic, or diatomic (II), e.g., O, S;
- (3) tribasic, or triatomic (III), e.g., N, P, As. Hence the three main types of compounds: I + 1, II + 2, III + 3 or the simplest representatives: HH , OH_2 , NH_3 " [7].

Special emphasis in this paper is laid on carbon: "Carbon, as may easily be shown, and as I shall explain in detail later, is tetrabasic, or tetratomic, i.e., one carbon atom ($C = 12$) is equivalent at four hydrogen atoms. The simplest compound with the element of the first group (H or Cl) will therefore be CH_4 or CCl_4 " [7]. To be precise, the conclusion concerning the CH_4 type was done by Kekulé even earlier [8].

As Kekulé himself states it, he arrived at the CH_4 type, and further at the idea of tetra-atomicity of carbon, from the Dumas theory of types when he studied various derivatives of marsh gas. The land-

* In 1855-1856, Wurtz established (by developing Williamson's idea of multiple radicals) that there were radicals of different atomicity: monatomic C_2H_5 and C_3H_7 , diatomic C_2H_4 , and triatomic C_3H_5 .

marks in his studies might have been conclusions from the theory of types by Gerhardt, e.g. the definitely determined atomicity of the radicals CH_3 or monoatomicity of other Gerhardt's radicals: CO(H) , formyl, $\text{CO(CH}_3\text{)}$, acetyl, etc. [2]. The formulas of these radicals contained (although in a masked form) the idea of tetra-atomicity of carbon, the more so that it was proved by the formulas of carbonic anhydride (CO_2) and marsh gas (CH_4) which had first been derived by Gerhardt. It is necessary to note that in his report to the Royal Institution, titled "On the Constitution of Hydrocarbons", Odling added the fourth type, CH_4 , to the former three types, HH , OH_2 , and NH_3 . It was in 1855, but the journal of the Royal Institution was, according to Anschütz, inaccessible to Kekulé who could not know anything about Odling's work [9].

It is, of course, difficult to establish now whether or not Anschütz was right, the more so that Kekulé himself could not deny Odling's influence on the formation of his idea of valency.

So 1857 was a kind of a summit point in the formation of concepts of atomicity of elements, of carbon in particular. In 1857, Kolbe, alluding to Frankland's work on the formation of organometallic compounds, proposed that formulas of all organic compounds should be derived from one type C_2O_4 (where the equivalent of carbon is 6 and of oxygen 8) by substituting oxygen equivalents in it. Frankland, in turn, alluding to this statement, maintained [10] that it had been Kolbe who introduced the concept of tetra-atomicity of carbon atom in 1857, although Kolbe himself did not at that time support the idea of atomicity; nor did he acknowledge the criteria of differentiation between an atom, a molecule, and an equivalent.

In 1850-1857 the idea of tetra-atomic carbon was in the air, and the concept of multi-atomic radicals, introduced by Gerhardt and Williamson and developed by Wurtz and Odling, inevitably led to the concept of valency. The main ideas of atomicity of elements, postulated in 1857 by Kekulé, were the first stones in the foundation of the valency theory.

Almost simultaneously with Kekulé, Cannizzaro also worked on the formation of the theory of valency. Ideas concerning this problem were spoken out by Cannizzaro in 1858 in his "Synopsis of Lectures on Chemical Philosophy". Cannizzaro's contribution to the theory is that he devised an objective method to determine atomic masses of elements, both metals and non-metals, and thus made it possible to establish correct valency of metals. A disadvantage of Kekulé's postulates of valency was erroneous ascribing univalent state to most metals. On the basis of his experimental data on density of vapour of various metal compounds, Cannizzaro disproved this Kekulé's proposition and proved that metals could be multivalent and present in various compounds in their different valent states.

So while Kekulé stimulated the determination of valency of non-

metals, Cannizzaro, almost simultaneously with Kekulé, made his contribution to the determination of valency of metals.

In 1858 Couper, Wurtz' disciple, published his paper "On a New Chemical Theory" [11]. The central in his paper is the problem of the structure of organic substances. He develops some ideas concerning the theory of valency and especially valency of carbon as a natural power to form chemical bonds.

Touching on the importance of valency ("grades of combination"), Couper wrote: "It is such a property that is required to form the base of a system. Nor would its suitableness for this purpose be affected by the discovery that the elements themselves are composite bodies, which view the chemist is perhaps not unwarranted to adopt" [11, p. 109].

Couper however had no clear idea of concrete valencies of elements, because he made use of equivalents. What was original in his paper, was the idea of electrochemical essence of affinity which is inherent in atoms of each element and shows itself in the form of valency. And he thought that the electrochemical properties varied depending on a particular partner with which a given element was bound.

The contribution of Couper to the development of the theory of valency is limited. First of all, Couper did not develop his ideas (because of his ill-health). Secondly, if we attach importance to his above mentioned work, we do it only in connection with the theory of chemical bond and chemical structure.

To summarize, we can state that a certain system of concepts of valency existed in 1858. It was based on correct chemical formulas of compounds of non-metals (Kekulé) and metals (Cannizzaro). These ideas originated from empirical material and were, both historically and logically, connected with the new system of atomic masses and chemical formulas of Gerhardt and Cannizzaro which was adopted at the First International Congress of Chemists at Karlsruhe (1860).

It is interesting to note that although the programme, which had been sent to the prospective participants, contained the problem of atomicity as an item on the agenda, it actually was not discussed at the Congress.

Anschütz wrote: "One may wonder why the problem of valency was not discussed at the Congress. The reason becomes clear when we remember that the fundamentals of the theory of valency are connected with the determination of atomic weights (masses,— *M. F.*), and it was this particular problem that was discussed at the Congress to the end" [9, p. 201].

The explanation does not seem satisfactory. Of course, the knowledge of atomic masses helps determine valency. But the concept of valency itself does not arise directly from the table of atomic masses. The problem of valency was not on the agenda of the Congress probably

because most of its participants, Kekulé included, did not attach great importance to this concept, whose significance became apparent a year later from Butlerov's report "On the Chemical Structure of Substances" ("Einiges über die chemische Struktur der Körper" [12]). The proof can be found in Kekulé's considerations on the program of the Congress. He wanted that the theory of types had been extended onto inorganic compounds [9, p. 186]. And although Kekulé connected the theory of types with the ability of atoms of an element to combine with one another at the expense of valency units, he regarded valency as an aid to explanation of the theory of types by Gerhardt [9, p. 186].

In 1860 the theory of valency was not important in the eyes of scientific opinion. We can conclude it from the decision adopted at the Congress in Karlsruhe: to consider equivalent as an empirical concept independent of the concept of atom and molecule. This decision shows that the chemists of that time did not see any connection between the concepts of "valency" and "equivalent", and thought it impossible that equivalents could be determined not only empirically but theoretically as well.

To end the discussion of the factual material connected with the history of formation of the concept and the theory of valency, we should like, for certain reasons, to dwell on the problem of priority in the formation of the theory of valency. Firstly, the solution of this problem will help better understand the ways of formation of the valency concept. Secondly, we thus can consider the historical and chemical material from various aspects. And thirdly, the problem of priority is closely connected with the problem of the place which the theory of valency occupies in the system of other chemical theories.

The problem of priority in the development of the theory of valency was raised late in the past century by Frankland and Kolbe who resolutely opposed Kekulé. Many historians of chemistry also dispute Kekulé's priority. For example, in his monograph "The History of Valency" [6] Russel writes that there were two ways in the history of chemistry which led to the formation of the concept of valency, and dedicates two chapters in his book to each of these theoretical trends, *viz.*, "From Radicals to Valency" (Chapter 2) and "From Types to Valency" (Chapter 3).

But we have already shown that Frankland came to his idea of the "combining power" of atoms not with the assistance but contrary to the theory of radicals, and that only after he had changed his position and supported the theory of types and the principles of the substitution theory, was he able to establish equivalence of alcohol radicals to oxygen equivalents. This led him to the recognition of the possible substitution of a positive radical for a negative oxygen: "The preparation and study of organic compounds containing metals,

Frankland wrote later, promises to reconcile these two theories (the theory of types and the theory of radicals,— *M. F.*) which have long been considered incompatible. For while it is quite clear that there are certain types of compounds, it is not less clear that the nature of a body deriving from the main type strongly depends on the electrochemical character of its component atoms and not only on the relative arrangement of these atoms" [5, p. 369]. Here Frankland means Dumas' theory of types. The new theory of types by Gerhardt accounts for the character of type and of radical [2, p. 271].

Thus Frankland had to give up the theory of Kolbe and the main propositions of the old theory of radicals to approach closely the concept of valency. And if he had not formulated the theory of valency by that time, it was only because he was overloaded with the old theory of radicals, in particular with the dualistic formulas of compounds and the related equivalents. Valency is the ratio of the atomic mass to the equivalent of an element. Correct valency can be found only from correct atomic mass and equivalent. This is why we cannot agree with Russel that the theory of radicals laid a straight logical way to the theory of valency.

Incorrect atomic masses and chemical formulas were obstacles to Frankland in his way to correct determination of valency, but, as Russel admits, this did not hold the English chemist from formulating a new concept of combining power. Russel compares Frankland with Boyle who was the first to enunciate the idea of a chemical element and did not discover any element. But this comparison cannot stand criticism. Boyle declined the alchemists' idea of the existence of the four elements* and introduced an entirely new concept, which was not contradictory to logics of that time, the concept of an element as a simple substance, i.e. a limit of chemical division; this was the turning point in the history of chemistry. Though Frankland conceived the new, he did not deny anything in the old theory and remained its prisoner.

In fact, Frankland's idea of the combining power or the ability of atoms to be saturated was not a new, revolutionary idea. First of all it was only a new expression of the old concept of chemical affinity of elements. Secondly, similar considerations had been earlier spoken out by Williamson, Odling, and others.

So we think there are no grounds to consider Frankland the founder of the theory of valency, as Russel states it [6, p. 117].

Russel gives much attention to the problem of priority in his book. He dedicates a whole chapter (Ch. 6) to this problem. At the beginning of this chapter Russel admits that in the history of the theory of valency "Kekulé is certainly the central figure, though not the only one" [6, p. 110]. Further Russel indicates that Kekulé

* Fire, air, water, and earth. (*Tr.'s note.*)

unjustly ignores (till 1890) any participation of Frankland in the development of the theory of valency and cites Kekulé: "If I am not mistaken, I was the first to introduce the idea of atomicity of elements into chemistry" [13].

In the same paper Kekulé names Williamson, Odling, and Wurtz as his precursors. The fact that he does not mention Frankland can be explained by that the latter resolutely supported the theory of radicals and made incorrect conclusions concerning the way by which the affinities of elements "are best satisfied".

In his lectures in the 1860s Frankland made attempts to claim his priority, but he did it very timidly, and his claims produced the reverse effect because Kekulé became very popular by that time because of his theory of structure of benzene. In 1877 Frankland made a more resolute claim. Referring to his paper published in 1852, he wrote: "It was evident that the atoms of zinc, tin, arsenic, antimony, etc. had only room, so to speak, for the attachment of a fixed and definite number of the atoms of other elements, or as I should now express it, of the bonds of other elements. This hypothesis ... constitutes the basis of what has been called the doctrine of atomicity or equivalence of the elements; and it was, so far as I am aware, the first announcement of the doctrine" [14].

This quotation is now interesting only because it definitely shows that Frankland regarded valency as the cause or the ability of atoms to form bonds.

In 1881 Kolbe published a series of papers under a common title "My Part in the Development of Theoretical Chemistry". The papers were later published as a separate book [15], where Kolbe supports Frankland's claims of priority, and attributes to himself the merit of formulating tetra-atomicity of carbon. Kekulé, in response, wrote an article "The History of Valency" and sent it to *Annals*. But following advice of Volhard, one of the *Annals* workers, he withdrew his paper and it was published only in 1929, by Anschütz [9]. In this paper Kekulé argues with Frankland and Kolbe. He produces objective arguments. In his book "August Kekulé", Bykov [3] gives these arguments in concise form and supplies his own comments. We also used some Kekulé's arguments in describing the role of Frankland.

Here we shall consider only one Kekulé's argument from "The History of Valency". He emphasizes that Frankland did not offer the theory of valency but only established the empirical regularity. Kekulé writes: "Frankland's law of satisfaction of affinity... is not connected with any hypothesis of the atomic theory" [9, p. 556]. Russel notes that in 1852 Frankland had no concept of the chemical bond, of the architecture of compounds. And this is why Kekulé, whose concept of valency was associated with the concept of chemical bond, reproaches Frankland with the absence of any hypothesis which could interpret the concept of valency. We think that Russel's

deciphering of Kekulé's criticism is correct in this case.

Later, in 1890, in his speech on the occasion of the 25th anniversary of the theory of structure of benzene, Kekulé mentioned Frankland's contribution to the development of theoretical chemistry as one of the leading supporters of the theory of radicals. He said that both trends, the radical and the type, tended to achieve one and the same aim though by different ways: "My views, he said in conclusion, originated from the views of my predecessors and were based on them" [16].

Frankland claimed his priority in the formation of the theory of valency till the end of his life, although he acknowledged the contribution made by Kekulé to the development of this theory.

The objective situation in the 1850s was as this: Gerhardt's reform led to the definition of the main concepts of the theory of atoms and molecules and to the derivation of correct empirical formulas of organic compounds. This promoted the formation of the theory of types by Gerhardt and established connection between equivalence of radicals and separate atoms, which had been initiated by Laurant, Williamson, Odling, and Gerhardt, continued by Frankland, and completed by Kekulé in the form of a system of the basic postulates of his theory of atomicity. So Frankland's ideas did not originate from nothing. They arose from the study of organometallic compounds. Frankland's failure is explained by that he had not made concrete conclusions concerning valency of elements and he had no valency unit, as affinity unit, at his disposal. Frankland's ideas might possibly be known to Kekulé but they were not the point from which he started on his way. Frankland, together with Williamson and Odling, was among the first to draw attention of the chemists (and this is his merit) to the different ability of elements to form compounds. Partington points this out as well [17].

The dispute about the priority in the development of the theory of valency shows that when the soil is ploughed by the preceding developments, new ideas can spring simultaneously in various countries and in different scientists, but not everyone is able to express these ideas clearly and to make the appropriate conclusions. Kekulé's contribution is that he not only introduced a new concept but also made concrete conclusions out of it. He revealed the importance of this new concept for the explanation of the formation of a homologue series of organic compounds, particularly by substantiating the general formula of hydrocarbons of the methane series, C_nH_{2n+2} .

2. The History of the Word "Valency"

The history of the term *valency* is also of interest. And we think this problem is important not only from the etymological aspect.

It is interesting to note that the first term that chemists used to describe the quantitative characteristics of affinity of atoms and radicals was "basicity" (not Frankland's "combining power"). Basicity was first introduced by Williamson in 1852 to characterize radicals as monobasic, dibasic, etc. [18]. In 1854-1856, Kekulé used this term as well, and later (1857) he offered another term "atomicity" (monatomic, diatomic atoms and radicals). In his work [10] Couper, in 1858, used the term the "degree of affinity" to describe the ability of the atom of an element to form compounds. But neither Couper's nor Frankland's term was accepted by chemists. In 1864, Odling offered the terms "monad", "dyad", and "triad" (monovalent, divalent, tervalent). Laurant (1846) used these terms as well but for a different purpose. Odling's terminology was not adopted either. Still another word appeared in 1858. This was "equivalence" and it related to isolated atoms. In this connection Odling writes that a hydrogen atom is characterized by one unit of equivalency and the atom of bismuth by three units [19].

In his textbook [20] published in 1865, Hofmann suggested that "atomicity" should be replaced by another term, "quantivalence" and that elements should be described as "univalent, bivalent, trivalent, and tetravalent in accordance with their atom-fixing capabilities" [20].

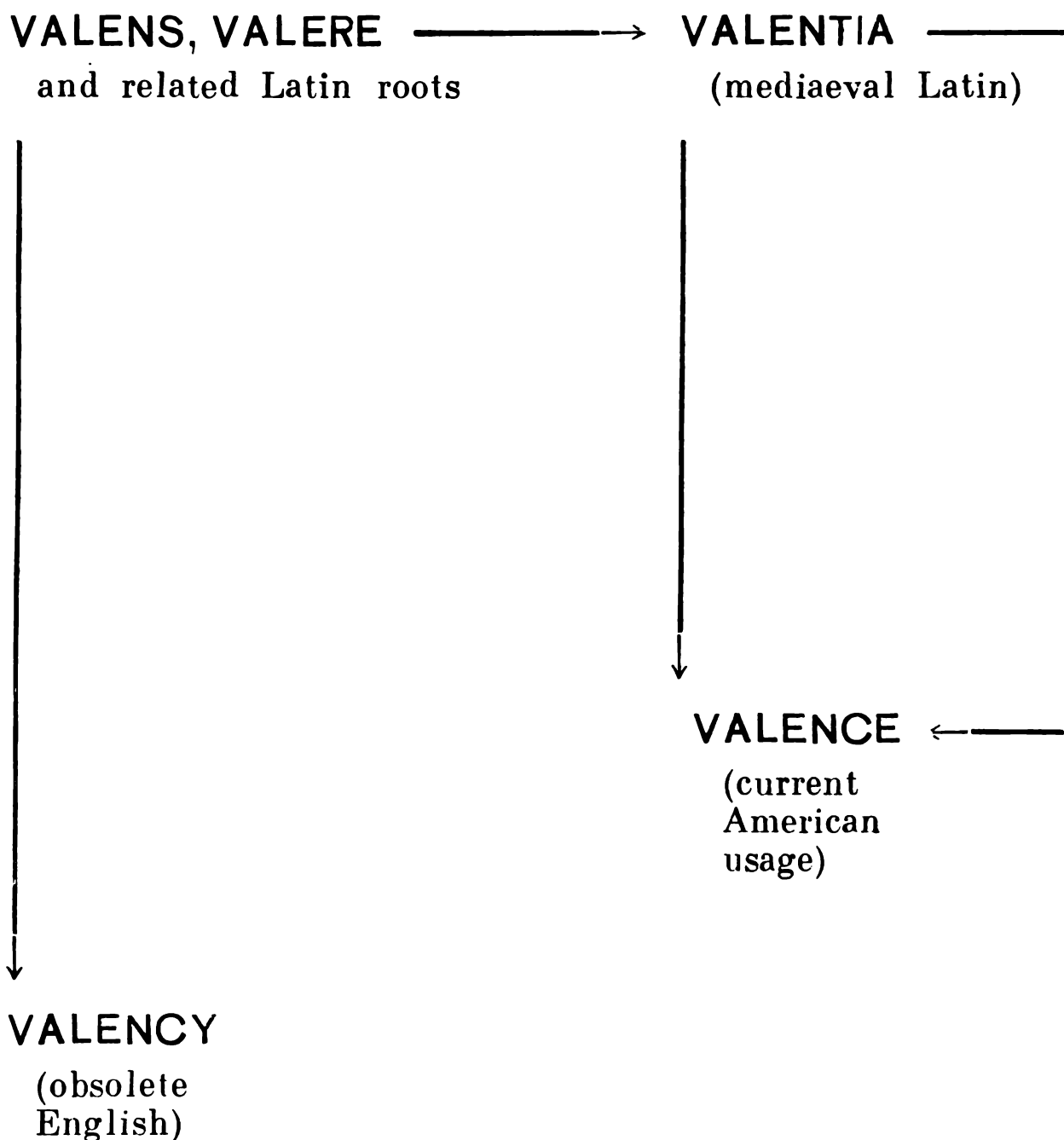
The term "quantivalence" was adopted in the English textbooks and journals. It was used by Roscoe (1871), Cooke (1874) and Stalo (1882), and in the Journal of Chemical Society (London) (up to 1885). And only Frankland, till 1866, along with his own term "combining power" continued using the term "atomicity", although later (1870-1877) he also used "equivalency".

But beginning with the end of the 1860s the term "valency" comes in common use in the chemical literature. First it appeared in Germany in 1867, in one of Kekulé's papers: "When I have gone to the trouble of explaining my views on atomic constitution of chemical compounds, he wrote, I have used for some years a method by which atoms of different valency (*valenz*) were represented by different size" [21].

Russel suggests that Kekulé, in private talks with his friends and collaborators, might have used the term "valency" instead of the cumbersome "quantivalence" [6] before 1867, i.e. long before he used it in the literature [21].

Later this term was used also by Wichelhaus, the disciple of Kekulé. He used it in his article published in March 1868, and then in his other paper in July of the same year. Wichelhaus explains this term as follows: "valency (*valenz*) is a shorter word for 'quantivalence' introduced with the same meaning by Hofmann" [22].

Russel [6] dwells on the etymology of the word "valency". He shows that this term was not borrowed directly from



Latin, and gives various meanings of the words which might form the root of the word "valency":

valens: *strong, powerful, energetic, able;*

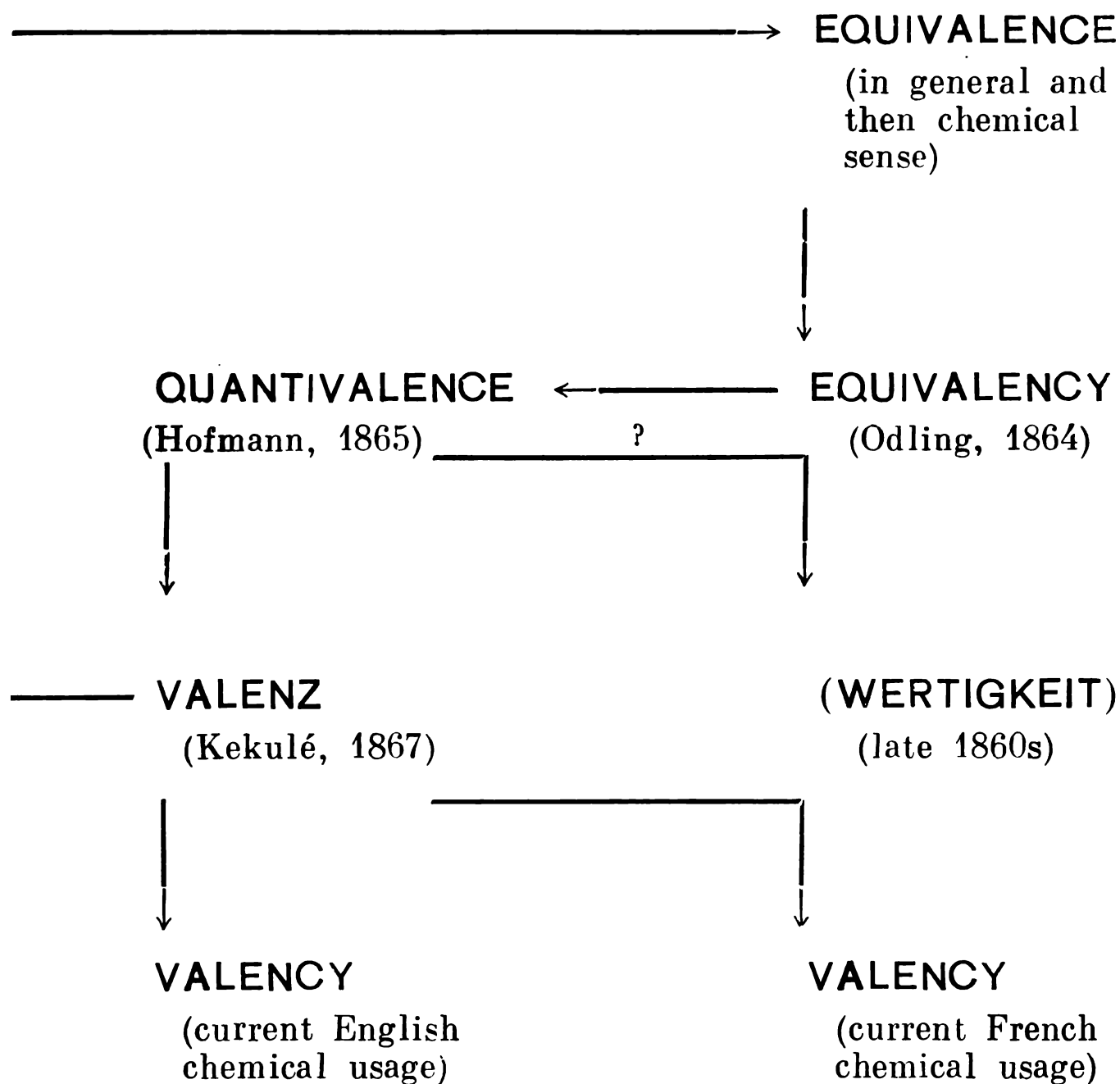
valere: *primarily to be strong or well; in a secondary sense to be worth;*

valentia: a mediaeval Latin term meaning *value*" [6].

As we have already shown, the term "valency" was introduced into chemistry by a different way. This way can be traced on the scheme taken from Russel's book [6] (see the scheme above).

The word *valency* came into the English chemical use in about 1869, and was completely adopted here in 1876 when it was entered into the *Encyclopaedia Britannica*. The term came into common use in the German and French languages in the 1870s as well.

The Russian pedagogical and scientific literature continued to use the terms atomicity and equivalence till early in the 20th century. All publications of Mendeleev's "Principles of Chemistry" (in Rus-



sian) contained the terms atomicity and equivalence. Mendeleev does not use "valency" in his works [23]. Butlerov uses the term atomicity [24]; N. A. Menshutkin uses "units of affinity" and "atomicity" in his textbook of organic chemistry [25]. A textbook of inorganic chemistry by Holleman published in Russian in 1909 also had atomicity and equivalence. And only the Russian translation of W. Ostwald [26] contained the term valency. Translations from the English had "valency" everywhere.

In his early publications, Chugaev used the "number of units of affinity" and "valency" [27], but beginning with 1913 he uses only one term, valency [28]. The merit of introducing the term valency into the Russian pedagogical and scientific literature almost undoubtedly belongs to Chugaev who was the highest authority in this field. At the same time, B. N. Menshutkin was the first in Russia to use this term regularly in the textbook of chemistry in 1924 [29].

From what we have said it follows that Frankland's "combining power" did not survive, while terminology offered by Williamson, Kekulé, Odling, Hofmann, and others (basicity, atomicity, equivalence, quantivalence, valency), connected with the theory of types, was acknowledged and the term valency adopted everywhere. This is another proof that the concept of valency has come into science through the theory of types and in the first instance through the works by Kekulé.

And finally, to end with the question of terminology, it is necessary to mention the term *chemical bond*. Some chemists of the past century mixed these two terms to give them one meaning: by valency they meant not only the *power of an atom* to attach a definite number of atoms of other elements, i.e. *the cause of the formation of chemical bonds*, but *chemical bonds themselves*, i.e. *the effect*.

3. The History of the Term "Chemical Bond"

The first, not quite clearly outlined concepts of chemical bond were proposed by Kekulé in 1857 when he showed that the "number of atoms bound (*verbunden*) with the atom of another element depends on basicity of the component parts" (atoms,— *M. F.*) [30]. In 1858, in addition to *verbunden* he uses also (and prefers) the words *Anlagerung*, *lagern* (adjoining) to express the formation of chemical bonds [12, p. 25-27].

In his paper "On a New Chemical Theory" Couper uses the term "to unite" to describe the formation of bonds between atoms [12, p. 38].

The term "chemical bond" was used for the first time by Butlerov in 1863 in his paper "On Various Explanations of Isomerism Cases", where he writes about "the method of chemical bond between atoms", and "*chemical bond* of separate atoms" [31].*

But Russel [6], for unknown reasons, writes that it was Frankland who first used the term "bond". In 1866 Frankland wrote: "By the term *bond*, I intend merely to give a more concrete expression to what has received various names from different chemists, such as an atomicity, an atomic power, and an equivalence. A monad is represented as an element having one bond, a dyad as an element possessing two bonds, etc. It is scarcely necessary to remark that by this term I do not intend to convey the idea of any material connection between the elements of a compound, the bonds actually holding the atoms of a chemical compound being, as regards their nature, much more like those which connect the members of our solar system" [32].

Thus Frankland actually identifies the term valency with the term bond, but Frankland's bond is different from Butlerov's chemical bond. Later, in his textbooks and scientific papers (1866-1877)

In the original, "*khimicheskaya sviaz*", where *sviaz* means bond. (*Tr.'s note.*)

Frankland emphasizes that it is impossible to conceive the nature of chemical bond.

It is interesting to note that beginning with the end of the 1860s the scientists of England reversed terms and used *valency* in the sense of chemical bond.

The confusion of the concepts of valency and chemical bond in Great Britain continued for a long period of time. In this connection, Friend offered in 1909 two terms to differentiate between the two concepts, namely "valency" which is the power (inherent in an atom) to attach other atoms, expressed by the number of univalent atoms capable of being attached, and "valence" which is the chemical bond between atoms in a compound formed as the result of the action of this power [33]. Some English chemists supported this proposition.

The question of terminological confusion is however connected with more significant reasons, namely with the absence of strict differentiation between valency and chemical bond. The point is that the idea of the existence of *certain causes*, responsible for combination of atoms in a molecule (composite atom), existed since Dalton's atomistic theory and was later developed in the theory of Berzelius. The unitary theory by Gerhardt, which was developed after the decline of the electrochemical dualism of Berzelius, promoted the formation of the concept of valency. This new concept established connection between empirical data on the composition and a purely hypothetic concept of chemical affinity. Kekulé [6] immediately associated the concept of basicity or atomicity with the idea of chemical bond to emphasize that atomicity is the numerical expression of the degree of affinity (*Verwandschaftsgrösse*) which is also determined by the number of chemical bonds of an atom. But as we have already said Kekulé did not use any special term to designate chemical bond and used the "unit of affinity" (*Verwandschaftseinheit*) to denote both units of valency and units of chemical bond [34]. Assuming that in explaining the properties of chemical compounds it is necessary to turn to "the elements from which these compounds are composed", and that he must proceed in this from his own earlier consideration on "the nature of elements, basicity of atoms", Kekulé was not quite consistent. He concluded by admitting that "since, in the exact sense of this word, scientific principles are absent, one must be satisfied with concepts based on probability and expediency" [12, p. 29].

Inadequate differentiation of the terms, and the confusion of atomicity and chemical bond could proceed from Kekulé's inability to imagine an atom outside a molecule; he therefore thought that atomicity-valency always shows itself as a certain number of chemical bonds.

Frankland, who first (1852) had used the terms "combining power" and "satisfaction of affinity" to express the inherent power of a free atom, later (1866) turned to use the term *bond* to denote both valency

and chemical bond. It was probably because he could not imagine valency of an atom outside a chemical compound either.

And it was only Butlerov who strictly differentiated the concept of atomicity, or the unit of chemical affinity of a free atom, from the concept of chemical bond.

4. Relationships Between the Concepts of Chemical Bond and Valency

Let us now discuss one of the main problems in the history of the theory of valency and chemical bond, viz., the problem of formation and development of ideas concerning the ability of atoms of one and the same element to combine with each other by affinity units, or valency units.

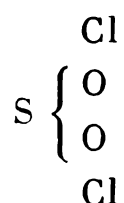
Of course it would be rightful to begin this discussion with Berzelius who was the first to indicate the necessity of clearing out the nature of chemical affinity, and who explained this nature by the action of electrostatic forces. But in our case we are more interested not in the qualitative characteristics of the affinity forces upon which the theory of electrochemical dualism by Berzelius was concentrated, but rather in their quantitative assessment, which was not given by this theory. We mean formation of chemical bonds as a result of mutual saturation of affinities which is the cause of chemical interaction proper. The idea of formation of chemical bond between atoms of one and the same element was revolutionary and contradicted the theory of Berzelius which was the dominating one at that time.

First ideas concerning the ability of atoms of one and the same element to combine with each other appeared in the works by Gerhardt and Laurant. It was substantially the revival of Avogadro's ideas who suggested that simple gases contain molecules consisting of two or more similar atoms [35]. These ideas were later utilized in the establishment of the composition of organic compounds, hydrocarbons in particular. Thus the "rule of parity", applied to the number of hydrogen atoms in compounds of carbon with hydrogen, formulated by Gerhardt, gave him grounds to deny the existence of radicals CH_3 , C_2H_5 , C_5H_{11} , which Kolbe and Frankland claimed to obtain in the free state. Gerhardt suggested that these formulas should be multiplied by two. Later, developing his theory, Gerhardt indicated (1852) that these compounds correspond to the hydrogen type H_2 , i.e. $\left\{ \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right.$ in which the radicals CH_3 , C_2H_5 , etc. are substituted for hydrogens, and hence the radicals (similar or different) must be connected with each other (like hydrogen atoms). Gerhardt wrote: "Hydrogen gas is hydrogen hydride, and chlorine gas is chlorine

hydride". Gerhardt regarded a molecule of nitrogen as the product of substitution of three hydrogen atoms in a molecule of ammonia by one nitrogen, and named it nitrogen nitride [36].

Perhaps they were Gerhardt's ideas that influenced Kekulé and led him, in 1858, to the conclusion of the existence of chemical bonds between carbon atoms. In his textbook of organic chemistry, Kekulé, in 1859, gave a graphic model of an oxygen molecule which consists of two oxygen atoms interconnected by two chemical bonds [37].

Proceeding from his original idea of the necessity to use "the nature of elements (i.e. their atomicity as the cause,— *M. F.*) to derive the nature of ... their compounds" (i.e. their composition and constitution as the effect), Kekulé does derive data characterizing a molecule from the valency of the component atoms [38]. As to the question, what particles can be formed by one atom of sulphur and two oxygen atoms, each of which has two units of affinity, he writes: "As the atoms touch, each unit of affinity of one atom unites with a unit of affinity of the other atom. Four of the six affinity units are thus used to hold three atoms together..." And Kekulé explains himself using a diagram [12, p. 24]: $S'' \begin{Bmatrix} O \\ O \end{Bmatrix}$. But two affinity units remain unused and "hence the group is diatomic; it can unite, for example, with two atoms of a monatomic element" [*ibid*]. And he gives another diagram:



These speculations about carbon atoms having four affinity units lead him to the idea that two out of the 2×4 affinity units of two carbon atoms are used for mutual saturation while the remaining six to attach monatomic elements, for example hydrogen. In this way he arrives at the general formula C_nH_{2n+2} for the homologue series of methane. And it can certainly be assessed as an important step towards the theory of chemical structure through deduction, i.e. by deducing the effect from the cause, the nature of a compound from the nature of the component elements.

Couper also considers the possibility of deducing the character of compounds from the properties of free atoms. "When all properties and faculties of *individual* elements are known we shall be able to clear out the constitution of compounds which are synthesized from the elements", he says [12, p. 34]. He thinks that valency, or "quantitative affinity of elements" is the "fundamental property inherent in all elements without which the element is devoid of its character and owing to which the element occupies its special place in the

composite body" [*ibid*]. And further, on the basis of the concepts of "chemical combination of carbon with itself", i.e. on the basis of the postulate of the formation of the carbon-carbon bond by mutual saturation of the affinity units of carbon atoms, Couper, from "the affinity and properties discovered in the elements", comes to his "theory of chemical structure". He also takes on the path of deduction, but ... only in principle. As we know Couper failed to create the working theory of chemical structure.

5. Butlerov's Contribution to the Development of the Theory of Valency

We shall not discuss here the main contribution that Butlerov had made to the development of chemistry by creating his theory of chemical structure, for we are interested now in those Butlerov's works which relate directly to the valency problem.

In his first paper dedicated to the theory of chemical structure (report at the 36th Congress of German physicians and naturalists at Speyer, Sept. 19, 1861) Butlerov, on the one hand, formulated his views concerning characteristics of valency of elements, and, on the other hand, chemical structure of compounds. "Each elementary share, says he meaning an atom, is given a certain amount of power which produces chemical phenomena (affinity). As a chemical compound is formed, part of this power, or its whole quantity, is consumed (bound, converted into a new form)" [31, p. 71]. Further he indicates that chemical affinity is expressed in whole numbers and assumes the affinity of hydrogen as the "minimum of this power".

The important point in these considerations is that Butlerov strictly differentiates between a free atom and an atom bound with another one, when its affinity is "bound, converted into a new form". Another important point is Butlerov's indication that in some cases the affinity units are consumed only partly and in other cases they are fully consumed. Here Butlerov does not admit the existence of the variable valency, since he regarded valency as a certain fixed number of affinity units inherent in an atom of a given element. At the same time this Butlerov's statement is a kind of explanation of the "variable valency" implying complete or incomplete utilization of affinity units inherent in each atom of an element. In contrast to Butlerov, Kekulé did not admit that affinity units can be utilized incompletely and always supported the fixed valency concept.

In the same paper the Russian chemist further emphasizes that "the quantity of affinity should be differentiated from its intensity—greater or smaller energy by which it binds substances. This intensity varies depending on the nature of the acting substances and on the conditions under which the action occurs" [*ibid*]. Here Butle-

rov differentiates between the quantity of free affinity, i.e. valency unit and the quantity of "bound, converted into a new form" affinity, i.e. the energy of bond formed by this unit or units. This postulate, which he derived from the analyses of chemical conversions, is the most important in Butlerov's theory, since it indicates the existence in a molecule of stronger and weaker bonds, i.e. the molecule reactivity.

Butlerov divides all elements into two groups, with odd and even valency. According to this division, atoms of elements with even valency can exist outside the compound. "The amount of free affinity, says Butlerov, is always an even number (0, 2, 4, etc.); hence an *atom* having two units of free affinity can exist independently, i.e. be a particle" [31, p. 72]. This statement is another proof that the creator of the theory of chemical structure regarded valency as the property of an atom in its pre-reaction state, while in a molecule he found both, completely (as in CO_2) and incompletely (CO) used affinities. "It can be assumed, says Butlerov, that a particle without free affinity, but certainly having at least two units of latent (consumed) affinity, decomposes at the moment of a reaction, and two units, which were formerly connected with each other in this particle, now combine with two affinity units belonging to a diatomic particle" [31, p. 72].

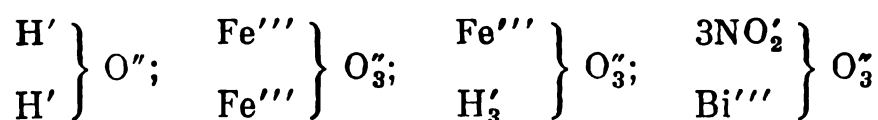
Here Butlerov, for the first time, formulated in the general form the idea of existence of latent valencies interconnected in pairs, which can fall in parts at the moment of a chemical reaction and combine with valency units of other elements. These ideas were later developed into the hypothesis by French chemist Delavaud and later by Frankland.

Like Kekulé, Butlerov differentiates between valency as the inherent property of elements and chemical bond as the manifestation of this property. But Butlerov's idea that a unit of chemical affinity (i.e. valency) converts into another form during formation of chemical bond and that there are unused paired affinity units, makes this difference more vivid and concrete. Butlerov regards valency of an atom as the force of affinity which is inherent in the atom itself and which is responsible for the "chemical phenomena". In other words Butlerov's idea is that valency of an atom is a certain potential power of the atom to form chemical compounds.

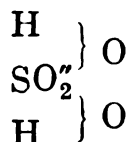
6. The History of Notation in the Theory of Valency and Chemical Bond

The first symbol to designate a unit of valency was offered by Odling who suggested that dashes should be superscribed at the right upper side of the symbols denoting atoms and radi-

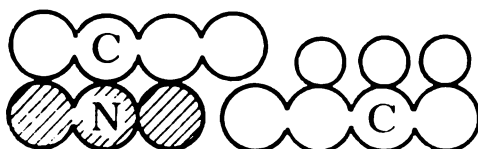
cals [39]:



Kekulé used this method in 1857-1858 [7] to express valency of radicals in typical formulas. When latent valency is concerned dashes express chemical bonds as well. For example:



where SO_2'' designates both the valency of the radical SO_2 and its two bonds with two hydroxyls. But in 1857-1858, in his lectures, Kekulé used his own models, where valency and chemical bond* were strongly differentiated. For example, he described methyl cyanide as follows:



The valency of the atom corresponds to the volume of the figure (the number of coalescing circle), while chemical bond is expressed by the touching atoms. These models express certain scientific concepts:

- (1) atoms remain unchanged after a molecule has been formed;
- (2) valency of atoms is fixed;
- (3) all valency units of atoms are equivalent;
- (4) all valency units are consumed in the formation of a chemical compound;
- (5) the adjoining position of atoms, which form bonds, is only conventional and does not correspond to any real, physical state (according to Kekulé);
- (6) these formulas (irrespective of the author's wish) express certain distribution of chemical bonds between atoms.

The graphic formulas, suggested by Kekulé, were used by other chemists as well, e.g. Wurtz (1864), Naquet (1865), and Blomstrand (1869). Odling's method was used by Butlerov to express valency of radicals (1863), by Frankland (1866), and others.

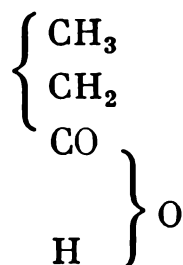
In the same year of 1861, when Kekulé offered his first graphic models, Loschmidt proposed another method: he used circles of different size which touch one another at the point of bond [37]. Loschmidt's formulas had a certain advantage over those of Kekulé and Couper.

The period between 1858 and 1863 was the turning point in the history of theoretical chemistry. This was the time when the theory

* These graphic models of molecules first appeared in 1861 in Kekulé's textbook [34, Bd. I, Teil 2, S. 165, footnote].

of chemical structure was at the stage of formation. The "typical" method of writing chemical formulas was therefore still used by many scientists, Butlerov included, but the old form already expressed new ideas.

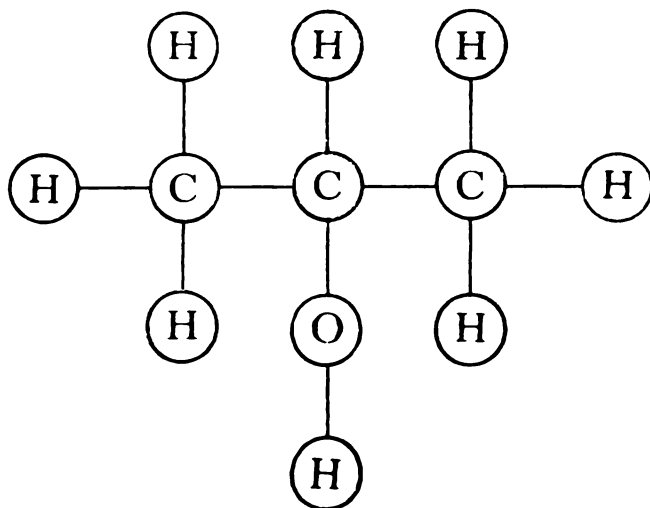
Butlerov wrote in 1861: "Time and experience will show what the formulas of chemical structure should look like. The formulas which are in current use now can in certain cases be used as well, but we must not associate them with the existing typical concepts. We got accustomed to see the expression of the typical concepts in these formulas and must therefore drop them, the more so that these formulas are cumbersome" [12, p. 53]. Butlerov, Markownikoff, and other Russian chemists used in 1860 a typical way of writing chemical formulas (using brackets) but they used them also to show the structure of compounds. For example, propionic acid was described by Butlerov as follows:



Brackets were mainly used to show chemical bonds between carbon atoms of the corresponding hydrocarbon radicals and their derivatives; the bracket uniting the groups CO, H, and O shows the hydroxyl group (in this formula) connected with the carbon atom of the radical CO.

In 1863 Butlerov used the typical way to express bonds in his chemical formulas; he also used dashes to indicate valency of radicals and Roman figures to express valency of separate atoms (S^{IV}, S^{VI}, C^{IV}) [31].

The modern method of linear representation of chemical bonds was offered by Crum Brown [40]. He placed chemical symbols inside circles, like this:

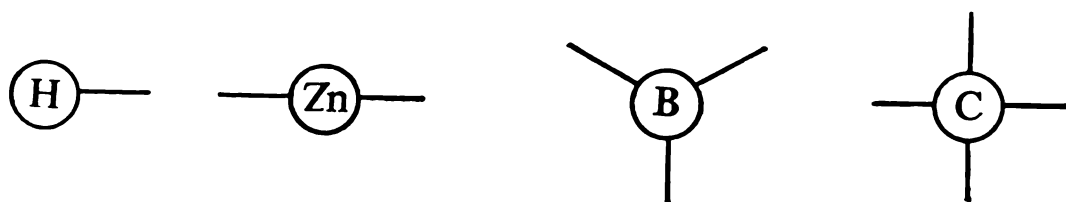


He wrote that in his formulas he did not mean to indicate the physical, but merely the chemical position of the atoms. This way of writing structural formulas was immediately adopted in England and only later in Germany. By 1870 this method was adopted almost universally.

In connection with the history of the linear representation of chemical bonds it is necessary to mention Couper's article (1858) which undoubtedly influenced Crum Brown, the more so that they were colleagues at the University of Edinburgh. Couper described chemical bonds by three dots (...) or a dash [11]. According to Wheeler and Partington, the history of this method can be traced back as far as to 1789, when Higgins used a line to show the union between two elements. Higgins's formula for water was $\text{I}-\text{d}$. Of course, this line does not mean here chemical bonds between atoms.

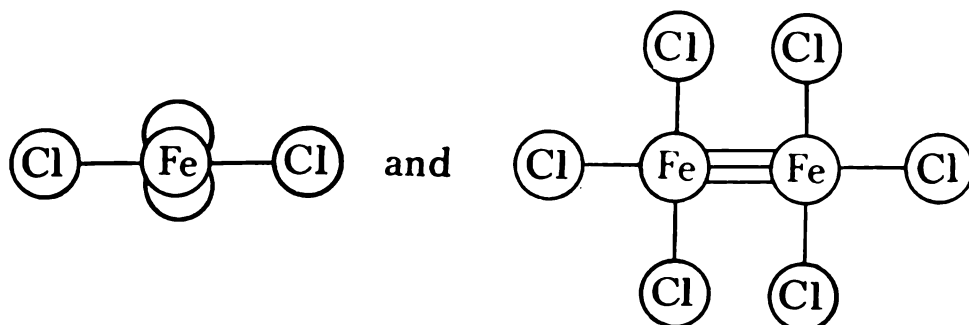
Crum Brown's formulas differed from Kekulé's graphic models by convenience of writing. Moreover, they could be used to predict isomers. It should be noted that Kekulé incorrectly predicted three isomers for propyl alcohol from his graphic formulas. In 1865-1866 Crum Brown and Erlenmeyer criticized Kekulé's graphic formulas, and in 1868 he himself gave up them [37, p. 269-270].

Frankland, in many respects, promoted the propagation of Crum Brown's models, and used them himself to show valency of free atoms. "To give a concrete expression to these facts, he wrote, the atom of hydrogen may be represented as having only one point of attachment or bond, by which it can be united with any other element, zinc as having two such bonds, boron—three and so on" [41]:



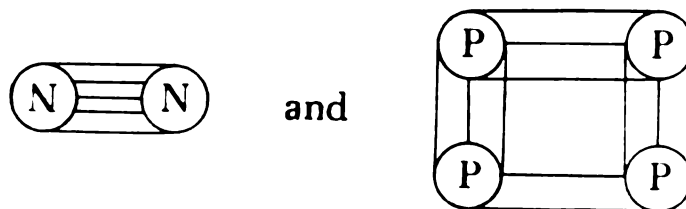
As is seen from the above designations, Frankland meant an unused chemical bond when he spoke about valency. Admitting variable valency and certain maximum valency for each atom, Frankland thought that in those cases where elements show their lower valencies, unused valencies saturate each other (just as Butlerov wrote in 1861).

For example, Frankland supposed that iron had the maximum valency of 6, and hence described iron chlorides as follows:



In the first formula four valency units are shown as arches above and below the symbol.

According to Frankland the molecules of nitrogen and phosphorus were as follows:



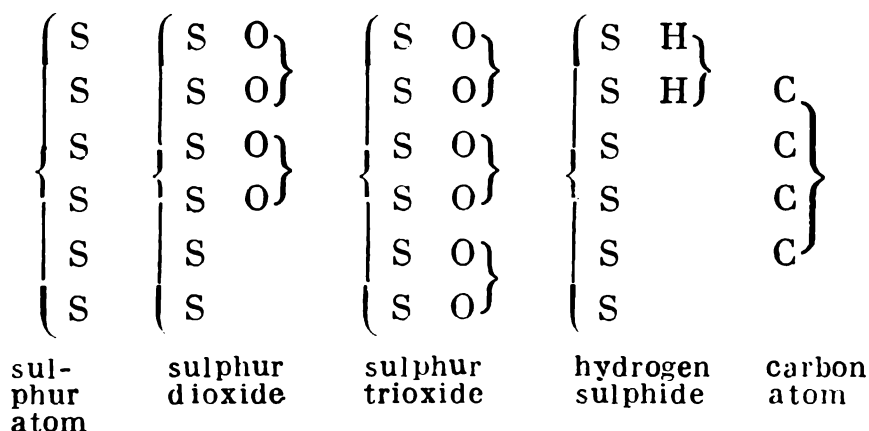
The new chemical formulas were soon adopted in England. In 1867 they were used without circles round the element symbols. First Kekulé [42] refused to accept Brown's formulas which he considered misleading in the sense that the bonds might be erroneously understood to be all in one plane. We know the answer of Crum Brown to this criticism: his intention was to show only *chemical* and not *physical* position of the atoms. In 1869 Kekulé acknowledged the advantages of the new chemical formulas and turned to use them [43]. In the 1870s the new formulas came into usage in other countries, Russia included.

7. First Attempts of Theoretical Explanation of the Nature of Valency and Its Regularities

Despite the fact that Kekulé's graphic formulas were merely didactic in their character, they played a certain role in the development of the valency concept. Showing the structure of molecule in the form of touching circles, Kekulé, whatever his intentions had been, indicated that each circle is a kind of a source of one unit of chemical affinity, i.e., that an atom consists of a certain number of parts (equivalents) which corresponds to its valency. Kekulé believed that all units of affinity of an atom are equal to each other, and are always saturated when the atom combines with other atoms, i.e. there are no free affinities in molecules.

Erlenmeyer held to the opinion that an atom of an element can have various numbers of affinity units, and at the same time be characterized by a certain maximum number of affinities (valencies). Erlenmeyer put it as follows: "Atomicity of an element is the sum of equivalents which *constantly belong to the atom* (italicized by M. F.), but with respect to various elements (and probably with respect to one and the same element) an atom can sometimes act as an integer, sometimes as a variable part of an integer, in accordance with the specific affinities of various elements" [44]. For example, he used a special method to describe compounds of sulphur with

other elements, where the symbol S did not express the atom of sulphur but only its equivalent, and O expressed the equivalent of oxygen ($S = 32/6$), ($O = 8$):



Erlenmeyer held erroneously that although the equivalents of carbon atoms are equal with respect to their mass, they have different affinity. Proceeding from this assumption Erlenmeyer thought that there are isomers of ethane, viz., dimethyl and ethyl hydride.

In 1861 Butlerov proposed his theory of chemical structure where he drew special attention to one of its main postulates, the one of energetical inequality of bonds between atoms. He maintained the postulate of non-equivalence of affinities. For example, he thought that two of the four affinity units of carbon are stronger than the other two affinities. Thus he explained the existence of CO_2 and CO , and the different strength of the $C-H$ bonds in CH_4 . But in 1862 he gave up this hypothesis and soon criticized it in detail. Erlenmeyer also stopped maintaining this hypothesis.

According to the modern concepts, valency electrons differ, as a rule, in energy (*s*, *p*, *d*, *f*-electrons). But in chemical compounds their energies are levelled (orbital hybridization), and similar atoms of other elements are therefore united with the given atom by bonds of equal strength.

An interesting attempt to explain some regularities of valency and to perceive the nature of valent bonds is the hypothesis by Charles Delavaud*. He, probably, formulated it not later than 1863, since Wurtz alluded to it in his "Course in Chemical Philosophy", published in 1864 [45]. Delavaud published a detailed description of this hypothesis in 1865 [46].

Discussing the elements with variable valency, Delavaud writes: "Why should we consider this atomicity as an abstract property of atoms, while we can attribute this property to atom constituents (*atomes constitutifs*) of a lower order." Further he gives the name of "sub-atoms" (*sous-atomes*) to these atom constituents and considers them carriers of valency units [46].

* Charles Delavaud was professor of organic chemistry at a naval medical school in Toulon.

There were difficulties in explaining variable valency in an atom of one and the same element. We have already mentioned that Butlerov explained this phenomenon by that affinity units are not always used completely during formation of compounds. At the same time Wurtz thought that each element has actual and latent valencies. For example, divalent atom of carbon in carbon monoxide becomes tetravalent in carbon dioxide because two affinity units, which "were dozing" before, got "awoke" now. This explanation seems less convincing than that given by Butlerov, the more so that Wurtz does not differentiate between valencies of free and bound atoms. Delavaud's objections to Wurtz are therefore quite reasonable. He considers Wurtz' explanation conspicuous but not satisfying our intellect. Delavaud gives an entirely different explanation: "The varying atomicity of a chemical atom ... is explained by that its constituents, or affinity units are connected between themselves" [46].

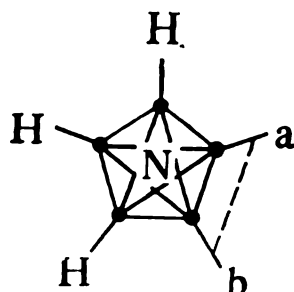
According to Delavaud, atomicity of an element always increases by two units, and even valency always remains even, and odd valency remains odd. This speculation leads Delavaud to an important conclusion: "Why do only two affinity units get "awoke"? Because sub-atoms (*sous-atomes*), which possess affinity, are connected in pairs. In the presence of a body which can react with these sub-atoms, combinations of identic sub-atoms are broken (*se defont*). Actually a molecule has no free affinity. Otherwise it would be impossible to explain why molecules with odd atomicity do not exist in a free state" [46].

Hence Delavaud declares that univalent radicals CH_3 , C_2H_5 and tervalent radical C_3H_5 cannot exist, while divalent radicals, e.g. C_2H_4 (ethylene) do exist. He tries to prove that the existence of NO and NO_2 , where nitrogen has odd free valencies (3 and 1), is not a deviation from the rule, and that the actual formulas of these substances are N_2O_2 and N_2O_4^* .

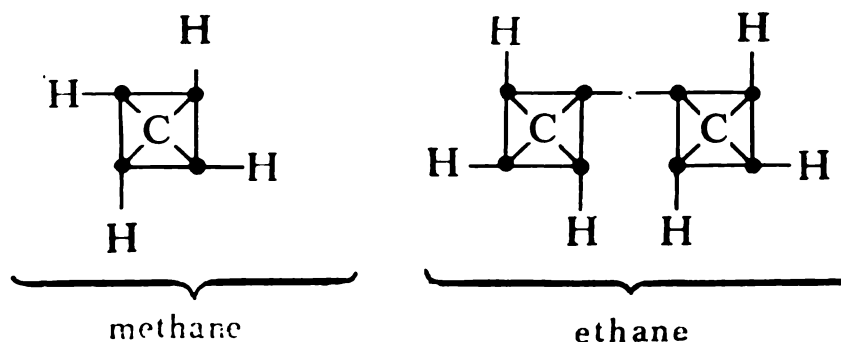
As we see, Delavaud's speculations agree with the modern concepts of instability of chemical particles with odd number of electrons.

Delavaud constructs his own models of various atoms and molecules. He describes an atom of nitrogen as a system of five interconnected sub-atoms. In a molecule of ammonia, three of its affinity units are saturated by affinities of hydrogen, while the remaining two (*a* and *b*) neutralize each other:

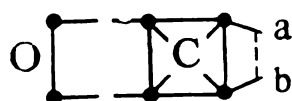
* Delavaud ascribed the maximum valency of 5 to nitrogen. To explain the correspondence of the molecular masses of said nitrogen oxides to those of NO and NO_2 with respect to relative density, Delavaud refers to Kekulé who distinguishes between "physical" and "chemical" molecules. So, according to Delavaud, the "chemical" molecules of these compounds are N_2O_2 and N_2O_4 .



Delavaud's models of methane and ethane are as follows:



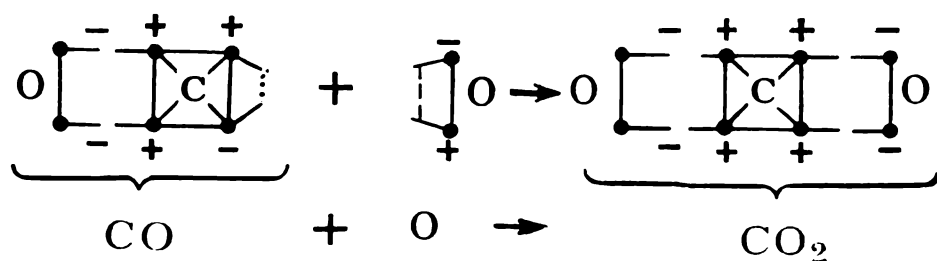
In carbon monoxide, two affinity units are mutually neutralized and two are saturated by affinities of two sub-atoms of the oxygen atom:



Delavaud writes: "If we try to establish analogy between chemical affinity and physical phenomena of polar character, magnetism in particular, then we shall have to compare each sub-atom with a magnet and each pair (of such sub-atoms) with a system of two opposite magnets, which agrees with Ampere's theory, developed by Wiedemann" [46, p. 428].

Thus, according to Delavaud, pairing of affinity units of sub-atoms in an atom of any element is magnetic in its character. He thought that "magnetic and electrical properties are the manifestations of a more general cause". The common character of magnetic and electrical forces, according to Delavaud, resides not only in their interdependence, but also in that they both are polar. He used the symbols $+$ and $-$ to indicate polarity of chemical forces of affinity. But he believed that this polarity is relative and can be alternated depending on particular interacting atoms.

For example, he described the reaction of carbon monoxide with oxygen as follows:



Delavaud emphasized that his views on the nature of valency differed from those of Wurtz and Kekulé. The latter, for example, did not admit that two affinity units of one and the same atom could be connected between themselves. Unlike Kekulé, Butlerov believed that affinity units of an atom could be mutually saturated.

Although well disposed to Delavaud's ideas in general, Wurtz however admitted only the existence of actual and virtual atomicity (*atomicité actuelle et atomicité virtuelle*), without disclosing the cause of this difference.

While assessing Delavaud's ideas from the point of view of the modern state of the valency theory, we must for a moment put aside the concrete details of his hypothesis and consider the general conclusions that can be derived from it. Delavaud felt by intuition that there exist certain regularities, which were later discovered and substantiated in the modern theory of valency.

The idea of a material carrier of the valency unit has now been proved. These carriers are valency electrons. The modern theory of spin-valency explains the existence of elements with odd and even valency (in the main sub-groups of the Periodic system by Mendeleev): this results from splitting of one, two, or several pairs of paired electrons with opposite spins. This theory reminds us of Delavaud's idea of disjoining paired sub-atoms.

Delavaud believed that the cause of pairing is the magnetic interaction between affinity units; and this idea has been proved valid as well. We know that paired electrons have opposite spins and opposite magnetic poles.

What was the attitude of Delavaud's contemporaries to his hypothesis? We have already mentioned Kekulé and Wurtz' attitude towards Delavaud. Other chemists (Naquet) considered this hypothesis as only speculative, and of course, they were right. Blomstrand's attitude to Delavaud's ideas is of interest. He thought it was prematurely to speak about carriers of valency units when it was not yet known if the assumed highest valency of a given element was actually the highest possible. He did not admit the existence of sub-atoms: "Mutual connection (pairing) of these minutest atoms has nothing in common with our ordinary concepts" [47]. Blomstrand explains the existence of elements with odd and even valencies in his own way: "To explain the possible existence of diatomic radicals (and radicals with even valency in general) I had to admit that there exists greater or smaller polarity of atoms, comparable with magnetic one. I had to admit also the existence of this property to explain regular changes in the saturability of two units" [47].

Blomstrand uses graphic models of atoms, which resemble those of Kekulé. For example, an atom with even valency is represented

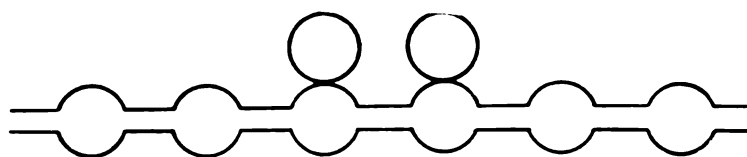
as this:



and with odd valency:



To explain why the elements of the oxygen group have only even valency, he writes: "This can be explained by comparing an atom with a magnet to which a positive pole of another magnet is brought close to a point located between the neutral centre and the negative pole, as a result of which the uniformity of the magnetic fluid is violated" [47]. When two univalent atoms are attached to an atom with even valency, the violated equilibrium is immediately restored. For example:



So, while Blomstrand does not formally admit divisibility of atoms into sub-atoms, his graphic representations of atoms with polar magnetic properties, which he ascribes to them, are nothing else but less definitely formulated ideas of Delavaud.

It should be noted that till 1966 the hypothesis by Delavaud was not duly considered in the chemical literature in this country or abroad*. In his book "The History of Valency" Russel does not mention this hypothesis but he cites Frankland (1866) on pages which are related indirectly to the hypothesis of Delavaud.

In connection with the rule of elements with even and odd valencies, which Butlerov mentioned in 1861 (Russel admits it), Frankland wrote: "These remarkable facts can be explained by a very simple and obvious assumption, *viz.*, that one or more pairs of bonds belonging to one and the same atom can unite, and, having saturated each other, become, as it were, latent. Thus the pentad nitrogen becomes a triad when one pair of its bonds becomes latent, and a monad when two pairs, by combination with each other, are, in like manner, rendered latent; and hexad sulphur becomes, by a similar process, successively a tetrad in triethylsulphine iodide and a dyad in sulphuretted

* This hypothesis was first revived in the book "From the History of Natural Science" [48] by the author of this chapter.

hydrogen" [49]. Russel cites the formula FeCl_2 from Frankland's textbook in which, as we have already said, four affinity units of iron form two latent pairs of mutually saturated bonds, while the remaining two are saturated with two chlorine atoms. Concerning these pairs of "latent atomicities", Russel writes: "The resemblance to modern formulae with unshared electron pairs is striking" [6, p. 188]. Further in his book Russel again remembers the hypothesis of Frankland as a direct precursor of the rule of odd and even valencies [6]. These notes, however, can to a greater extent be referred to Delavaud who proposed and published his hypothesis before Frankland.

Russel tries to explain why ideas of Frankland and Delavaud did not impress their contemporaries. In Russel's opinion this is explained by the discovery in 1860-1870 of many transition metals (V, Nb, W) which do not obey the rule of odd and even valencies. Russel indicates that supporters of the fixed valency concept did not recognize the existence of latent atomicities. These speculations of Russel are to a certain degree motivated. But the cause why the interesting ideas of Delavaud and Frankland were not recognized is probably seated deeper. Late in the 1860s the theory of atom was disputed by many chemists and if some of them acknowledged it, they considered it only as a working hypothesis. This is why the hypothesis by Delavaud, which was based not only on the admission of the existence of atoms but even of sub-atoms, and also Frankland's concepts of paired units of abstract chemical affinity belonging to dubious atoms, could not be easily accepted at those times.

Thus the first attempts to conceive the nature of valency gave rise to the first, although naïve concepts of complexity of the atom. Using only purely chemical methods chemists came to a conclusion that there exist particles less than atoms.

Thus we meet with the first models of the atom structure which were quite speculative at that time.

8. The Problem of Constant and Variable Valency

For the object which we pursue in this chapter, the problem of constant and variable valency is not very important. The fact is that all who assumed valency to be the basic inherent property of an element, who regarded it as the quantitative characteristic of potential ability of an atom for chemical combination with other atoms (and they were almost all chemists who took part in the development of the theory of valency) considered that this problem was essentially whether or not all affinity units of a free atom are used during its combination in a molecule.

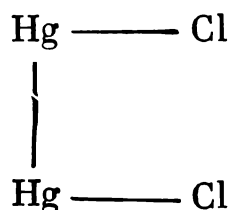
But this story is deductive in general and its discussion gives additional material concerning the history of the theory of valency.

Of greatest interest is the critical analysis of the theory of constant valency since those who supported this theory, along with speculative arguments, gave many important propositions which were proved valid experimentally.

The two approaches to the concept of valency were formulated at the very birth of the theory of valency. Frankland and Couper and some others suggested that there exists variable valency. Kekulé, Foster, Wichelhaus, and other chemists supported the idea that valency can only be constant.

Kekulé, who came to his theoretical conclusions concerning valency through the theory of types, and hence from the study of compounds of non-metals with hydrogen, naturally thought that valency of elements is fixed, and attains its maximum of four in carbon and silicon. He defended his concept as follows: valency is the inherent quantitative expression of chemical affinity of an element and it must be as constant as its atomic mass.

As a rule, valency which Kekulé ascribed to elements was not the maximum possible, but on the contrary their minimum: 1 for halogens, 2 for sulphur and its analogues, 3 for nitrogen and its analogues, and 4 for carbon and silicon. According to Kekulé, during formation of any compound, all affinity units are used completely to form chemical bonds; he did not admit the existence of free affinity units. The cases where valency of elements was less than the discovered maximum Kekulé explained by the formation of multiple bonds, or chains. The importance of Kekulé's idea of multiple bonds is obvious: it was later developed in the theory. Less fruitful was the idea of formation of chains. For example, Kekulé thought that mercury is divalent, and explained indications to the existence of univalent mercury as follows:

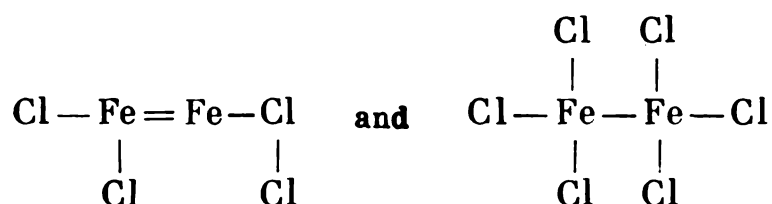


The idea is not at all fruitless and is supported by the compounds of the type $\text{R}-\text{O}-\text{O}-\text{R}$, $\text{R}-\text{S}-\text{S}-\text{R}$, etc.

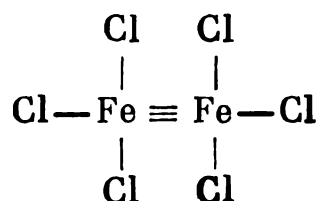
In cases where valency turned out to be higher than Kekulé supposed it to be, he admitted the formation of molecular compounds. For example, PCl_5 , NH_4Cl , SeCl_4 were molecular compounds to Kekulé: $\text{PCl}_3 \cdot \text{Cl}_2$, $\text{NH}_3 \cdot \text{HCl}$, $\text{SeCl}_2 \cdot \text{Cl}_2$. Probably this idea was not fruitless either. Sometimes it was proved valid, e.g. in $\text{NH}_3 \cdot \text{H}_2\text{O}$.

Postulation of obligatory consumption of all affinities naturally led to insolvent explanations. For example, Friedel believed that iron is a tetravalent atom (from the formula of pyrite, FeS_2) and there-

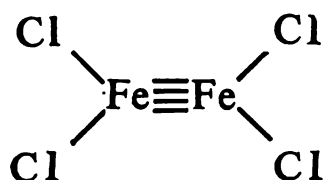
fore gave the following formulas to iron halides:



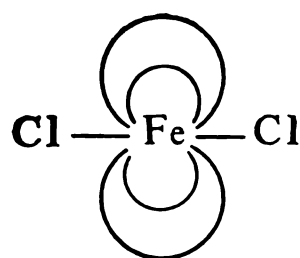
Wurtz used the same formulas. Odling and Frankland held that the maximum valency of iron is six, and hence the formula of iron chloride is



These chemists actually extended the concept of multiple bond from organic chemistry to inorganic compounds. But for ferric chloride they probably did not dare give the formula



but returned to the idea of mutual saturation of affinities



The Italian scientist Sestini [50] held that true formulas of ammonia and nitric oxide are the following formulas with multiple bonds: $\text{H}_3\text{N}=\text{NH}_3$ and $\text{O}=\text{N}\equiv\text{N}=\text{O}$, although such a statement contradicted the experimental data on the density of these gases. Sestini tried to justify his formulas by Kekulé's hypothesis of "physical" and "chemical molecules" and thus actually gave another proof of insolvency of these Kekulé's ideas as applied to gases.

In contrast to the theory of constant valency, which wanted by all means to give home to each affinity unit so that none of them remained free, the theory of variable valency postulated a step-wise consumption of the maximum valency or maximum of affinities which pre-exist in an atom of a particular element. The steps, or degrees of consumption of affinities of an atom depend on the reaction conditions

and the nature of the atoms which take part in the formation of a molecule.

We shall not dwell on this theory, and should like only to emphasize that all supporters of the constant valency theory can be divided into two groups: one group consisted of those who admitted incomplete consumption of affinities and the existence of unused free units, and the other group who considered that incompletely used affinities could be mutually saturated inside one and the same atom.

The theory of variable valency has been proved valid experimentally. The study of the composition and properties of organic derivatives of sulphur, nitrogen, phosphorus, and other elements has proved that valency of these elements can vary as follows S—2, 4 and 6; N—3 and 5; P—3 and 5.

The variable valency theory has offered wide possibilities in the study of various manifestations of the reactivity of atoms of any element. The theory postulates the following:

(1) Each element differs in this or that way from any other element in the periodic table by its chemical properties, these differences residing in strictly specific valency potentialities of a given element, upon which its identity depends.

(2) The display of these potentialities in the process of a chemical reaction depends on the nature of other elements with which it forms chemical bonds.

Some important conclusions can be derived from these postulates:

(a) valency should in principle be regarded as the reactivity of an atom of a given element;

(b) characteristics of the reactivity should systematically be enlarged by new data concerning the internal structure of the atom and its possible combinations with other atoms;

(c) information concerning the reactivity of atoms of chemical elements should, in principle, help deduce conclusions on the structural characteristics and properties of the compounds formed.

In addition to the former two approaches, there existed the third approach to the concept of valency in the 19th century. According to this approach it was impossible to characterize any property of a chemical element until it combined with other elements into a substance.

In the 1880s, Lossen rejected the idea that the atoms of elements have pre-existing valency. Lossen suggested that the concept of valency only be used to describe atoms combined in molecules. But the structural characteristics of molecules, especially multiple bonds, were first derived from the assumption of tetravalency of carbon, and he therefore denied the existence of multiple bonds in unsaturated organic compounds. Lossen wrote: "The bond between the atoms in the molecule of acetylene $\text{H}-\text{C}-\text{C}-\text{H}$ becomes clear to understand if we admit that it contains two divalent atoms of carbon." The bonds

in the molecule of benzene can be explained similarly if we assume that it contains six tervalent atoms of carbon, each connected with one atom of hydrogen [51]. Lossen thought that molecules of oxygen and nitrogen also had only one bond. Lossen's general principle was as follows: "The atom value (*Wert*) is the number showing how many atoms are found in the binding zone" [51, p. 288].

Some other chemists, e.g. Chichibabin, supported this principle. Chichibabin believed that carbon in benzene is tervalent and denied the presence of multiple bonds in aromatic molecules.

Klaus [52] was also of the opinion that the atom has no pre-existing valency units and that the hypothesis of valency is "unnatural" and "unfounded". But his objections were mainly directed against the interpretation of valency as a characteristic expressed by whole numbers rather than against the theory which postulated valency as one of the main properties of an isolated atom.

The idea that chemical affinity of an atom is integral in its character and that the atom has neither pre-existing "points of attachment" nor units of affinity, and finally that chemical interaction causes the formation of a certain number of bonds with other atoms, was suggested by Werner (see Chapter 4).

So we can summarize that the evolution of the theory of valency has led, on the one hand, to concrete concepts of valency as one of the main characteristics of the atom, and, on the other hand, even to rejection of valency as something pre-existing. The theory of Kekulé, which arose as the generalization of chemical data, stimulated the formation of the concept of chemical bond as a manifestation of "pre-existing" valency. But 30-40 years later, some outstanding scientists revised the theory. They postulated that the chemical bond is something self-contained, and valency is the number of chemical bonds determined by purely empirical methods from the composition or the conjectured structure of a given molecule; they admitted the existence of only one bond between two atoms.

These ideas were not widely propagated. They were the result of the first attempts to explain the structure of molecular compounds which could not be explained by the theory of constant valency of the elements.* At the same time, they to a certain degree reflected the general tendency of "reappraisal of values" or, at least, of a significant change in the assessment of the role of the valency theory. During formation of structural theories this role was regarded by Kekulé, Couper, and Butlerov as dominating and was not disputed by anyone. But when the structural ideas began flourishing the gravity centre of the research was shifted to the chemical bond and to the atom as the centre-point of this bond. And the main attention was now given to the properties and the state of an element

* Chapter 4 is devoted to this problem.

bound in a molecule. The main trend in earlier research had been the study of properties of chemical elements themselves grouped in series, or in a system of elements. But with the advances in structural chemistry, the main attention was given to the state of bound elements and the reactivity of elements as fragments of molecules. This is why, in the 1880-1890s, valency was mainly regarded as the valency state of the atom in the structure of molecules rather than valency possibilities of atoms of a given element.

But this new tendency did not mean that structural chemistry put an end to the study of chemical elements as such within the boundaries of their system. On the contrary, the wealth of the material illustrating the numerous variations in valency potentialities of an atom of one and the same element (depending on the partners in the reaction) gave a new impetus to the studies of potential reactivity of elements themselves. The information on the structure of molecules, and on the chemical bond now played the main role in widening the knowledge of causes of chemical bonding, i.e. valency potentialities of the atom. It is expedient therefore to consider the relationships that were developing between the concepts of valency, affinity bond, and chemical structure.

9. Relationships Between the Concepts of Valency, Chemical Affinity, Chemical Bond, and Chemical Structure

The problem of chemical affinity was always one of the central problems in chemistry. Affinity was given different interpretations in various periods of history. It depended on advances in physics. In the seventeenth century, chemical affinity was regarded as something mechanical, like hooks and loops; in the eighteenth century it was understood as something dynamic, for example, as a display of the universal gravitation law; early in the nineteenth century, Davy put forward his electrochemical theory, which was later developed by Avogadro, and then Berzelius [2]. The search for quantitative criteria of affinity was begun in the eighteenth century. The first step in this direction was the determination of the "combining weights" (Bregman and others). In the first half of the nineteenth century quantitative characteristics of affinity were sought for in the electrochemical properties of elements. Avogadro noticed that there is an indirect connection between the volume of the atom and its electrochemical properties, and showed that the positive charge on the atom increases with its volume.

The decline of the electrochemical dualism and the development of the unitary theory did not solve the problem of chemical affinity but only rejected its electrochemical interpretation. The new trend only

admitted that elements and radicals with opposite chemical action can exist and they should be marked with positive and negative symbols. The symbols were rather conventional.

The emergence of the valency theory gave a great impetus to further development of the concept of chemical affinity. Although this concept remained at the phenomenological level, the theory of valency gave a quantitative approach to it, which was a step forward towards the disclosure of its physical essence.

All papers published in the 1850-1860s regarded valency as a property pre-existing in a particular element, which, along with the atomic mass, makes this chemical element different from all other elements and which can be expressed by a whole number of affinities of the atom of this element.

The valency concept stimulated the emergence of a new scientific concept, that of the chemical bond. Kekulé and Butlerov were the first who derived the concept of the chemical bond from valency. Thus valency turned to be the expression of other two concepts. It served not only as a measure of chemical affinity but also as a measure determining the number of chemical bonds. And valency itself was determined from empirical formulas of simple inorganic compounds. This imparted a character of objectiveness to valency.

Along with the emergence of the variable valency concept, there appeared another concept of its different manifestation. In addition to valency as a pre-existing property of a free atom, there appeared the concept of valency as the state of a bound atom. The former was regarded as the maximum possible valency, and the latter as its realized part. The first strictly outlined postulates were given in 1861 by Butlerov in his eight rules of formation of chemical compounds [31, p. 71-73]. In 1864-1866, Wurtz [45] and Frankland [49] drew special attention of chemists to the differences between valency potentialities and the valency state of an atom. Wurtz believed that a bound atom has actual and latent (potential) valencies. According to Wurtz the former are valencies realized in the form of chemical bonds, while the latter are unused valencies. Frankland differentiated between absolute, actual, and latent valencies. According to Frankland (as well as Delavaud) latent valencies are mutually saturated in pairs. Erlenmeyer held approximately the same views [44].

Thus the adherents of variable valency assumed that each atom bound in a compound has two forms of valency, viz., valency potentialities and valency state. They suggested that all valency potentialities are used in saturated compounds and that free atoms have only valency potentialities. But as the theory of atoms and molecules triumphed, it appeared that even simple substances consist of molecules in which homoatoms are bound by valency units. Now

the concept of existence of free atoms with only valent potentialities appeared to be purely abstract in character.

The defenders of the theory of constant valency could not imagine atoms with residual valencies. They recognized only valency states, and explained the increasing valency index (n) in chemical formulas of compounds of the AB_n type (compared with the valency assumed for A) by the formation of chain bonds between atoms of one and the same element.

Practical use of valency as a quantitative measure of chemical bond immediately encountered with difficulties. Butlerov was the first to indicate them. As he studied butylene and its derivatives, and also various compounds containing methylene group, Butlerov showed that even if the valencies of the elements are known to a chemist, he cannot speculatively solve the problem of actual chemical bonds. To solve this problem, the chemist must know the physical and chemical properties of a particular compound, which alone can help establish the structural formula. Butlerov showed the necessity of accumulating empirical material from which a rule could be derived. And he indicated that the theory of valency, though being the fundamental concept of the theory of chemical structure, is unable to give a simple answer to the question how the chemical affinity of each atom is distributed among the other atoms in a molecule. Moreover, the classical theory of valency could not explain why the compound CO exists, while CH_2 or CCl_2 do not.

Another, even greater difficulty arose, as we have already shown, in connection with the two approaches to the valency concept (constant and variable valency concepts). To Kekulé and other adherents of the former concept, valency ceased to reflect real facts and disagreed with empirical formulas. Moreover, in the solution of the problem of structure of organic compounds, the supporters of the constant valency theory used this concept to solve the problem of the chemical bond. But they gave up this principle when the structure of inorganic compounds was concerned. They used the concept of the chain-like structure of organic compounds to justify valency numbers which they themselves gave to the elements. Thus chemical bond became the cause instead of the effect. Without knowing it, Kekulé and his supporters undermined the fundamentals of the valency theory: by using various speculative structural formulas they made it possible to justify any valency.

Another important problem that remained unsolved by classical chemistry was the relationships between the unit of valency and the unit of chemical bond. But is it rightful in general to use the concept of chemical bond? Are all bonds, formed by saturation of two affinity units, equivalent by their strength?

There exists an opinion that according to the law of equivalents all simple chemical bonds must be equivalent. This is not so. Firstly

the law of equivalents was formulated early in the nineteenth century, when there was no theory of valency or chemical bond, and this law could not give any grounds for such a conclusion to be made. But even later, in the second half of the nineteenth century, this conclusion could not be made either. The chemical equivalence of elements in substitution or combination reactions does not confirm equivalence of chemical bonds by their strength. A reverse conclusion could be made only on the condition that the chemical affinity of various elements having the same valency could be assumed to be equivalent. But chemists never insisted upon it. They never claimed that the affinity of a chlorine atom is equivalent to the affinity of a hydrogen atom, or that the affinity of a sulphur atom is equal to that of an oxygen atom, or else that the affinity of a nitrogen atom is the same as that of a phosphorus atom, etc. ...

At the same time we have to admit that Kekulé tacitly favoured the propagation of the concept of equivalency of units of chemical bond. First of all, by valency he meant the magnitude of chemical affinity (*Verwandschaftsgrösse*); chemical bond, formed by a unit of valency, he called a unit of chemical affinity. Moreover, he offered graphic models of atoms of various elements. These were combinations of fused balls of equal volume whose number corresponded to the number of valency units. All this helped develop an opinion that valency is a direct measure of affinity.

There was another problem in classical chemistry concerning the magnitude of the affinity unit in one and the same atom. We have already said that Butlerov (in 1861-1862) assumed that the affinity units of a carbon atom might be different, but soon he gave up his opinion and proposed a thesis of mutual effect of atoms by which he explained inequality of the energy of chemical bonds. Erlenmeyer held to this opinion till 1863-1864. As late as in 1869, Blomstrand maintained that not all affinity units of a nitrogen atom are equal. But Butlerov's concept of mutual effects of atoms, as the only possible explanation of inequality of chemical bonds, finally triumphed. His concept was further developed by Markownikoff (in 1865 and later) [53]. Thus Butlerov and Markownikoff not only differentiated between the concepts of valency and chemical bond but also put forward the idea of atom changeability depending on whether it is unlinked (possessing only valent potentialities with residual and invariable chemical affinity) or bound, when these potentialities are realized.

The energy of chemical bond has a direct relation to chemical affinity of elements and their interactions. But the concepts of this relation were constantly developed and changed. Suffice it to say that, at various periods of the history of chemistry, by affinity were meant various types of mutual attraction of atoms, and the energy of formation of compounds. At the time when valency was regarded

as the number of affinity units of an atom, the term affinity was understood as the unknown but obviously discrete forces (or particles) which are present in an atom and make it aggregate into a molecule. These "forces" are known now. This is the interaction of the atomic nuclei and valency electrons. But only a decade or two ago, by affinity chemists understood something quite different, namely, the heat of formation of compounds, or Gibbs' potential. If we compare now the modern concept of affinity with Kekulé's concept of valency as a unit of some other affinity, we shall have nonsense. The point is that, for example, the affinity of oxygen for hydrogen is rather high (the energy of formation of water) while the valency of oxygen by hydrogen is only two. At the same time, the affinity of chlorine for oxygen is insignificant, while its maximum valency by oxygen is seven.

The relationships between affinity, valency, chemical bond, and energy of chemical bond became more or less clear only after quantum mechanics has revealed the essence of chemism and established quantitative relationships between the energy of formation of a chemical particle from atoms, on the one hand, and the structural electronic-nuclear characteristics of these atoms, on the other hand. But to attain this stage of understanding, chemistry had to pass a long way through phenomenological theories describing unsaturated and then complex compounds, the theory of periodicity, and many pre-quantum electron theories.

References

1. *Correspondance de Ch. Gerhardt*, v. 1., Paris, 1918, p. 342.
2. Fayershtein, M. G., *The History of Molecule*, Academy of Sciences Press, Moscow, 1961, p. 263-265 (in Russian).
3. Bykov, G. V., *August Kekulé*, Nauka, 1965, p. 49 (in Russian).
4. Frankland, E., *Phil. Trans.*, 1852, v. 142, p. 417-444.
5. Frankland, E., *Ann.*, 1853, Bd. 85, S. 329.
6. Russel, C., *The History of Valency*, Oxford, 1971.
7. Kekulé, A., *Ann.*, 1857, Bd. 104, S. 129-150.
8. Kekulé, A., *Ann.*, 1857, Bd. 101, S. 200-213.
9. Anschütz, R., *A. Kekulé. Leben und Werken*, Bd. I, Berlin, 1929, S. 109.
10. Frankland, E., *Proc. Roy. Soc.*, 1865, v. 14, p. 198-204.
11. Couper, A., *Phil. Mag.*, 1858, [4], v. 16, p. 104-116.
12. Centenary of the Chemical Structure. Collection of papers by A. M. Butlerov, A. S. Couper, A. Kekulé, and V. V. Markownikoff, Publishing House of the USSR Academy of Sciences, Moscow, 1961 (in Russian).
13. Kekulé, A., *Comp. rend.*, 1864, v. 58, p. 510-514.
14. Frankland, E., *Experimental Researches in Pure, Applied and Physical Chemistry*, London, 1877, p. 145.
15. Kolbe, H., *Zur Entwicklungsgeschichte der theoretischen Chemie*, Leipzig, 1881. 117 S.
16. Kekulé, A., *Ber.*, 1890, Bd. 23, S. 1302-1311.

17. Partington, J. R., *A Short History of Chemistry*, London, 1939, p. 285.
18. Williamson, A., *J. Chem. Soc.*, 1852, v. 4, p. 353.
19. Odling, W., *Phyl. Mag.*, 1858, v. 16, p. 40.
20. Hofmann, A. W., *Introduction to Modern Chemistry*, London, 1865.
21. Kekulé, A., *Z. Chem.*, 1867, [2], Bd. 3, S. 214.
22. Wichelhaus, G., *Ann.*, 1868, Suppl. Bd. VI, S. 257-280.
23. Mendeleev, D. I., *Fundamentals of Chemistry*, 8th ed., 1906, p. 168 and 230 (in Russian).
24. Butlerov, A. M., *Journal of Russian Physicochemical Society*, 1879, v. 11, p. 289-311 (in Russian).
25. Menshutkin, N. A., *Lectures on Organic Chemistry*, 3rd ed., St.-Petersburg, 1897 (in Russian).
26. Ostwald, C. W., *Principles of Chemistry*, Moscow, 1910, p. 293.
27. Chugaev, L. A., *Selected Works*, v. 1, Academy of Sciences Press, Moscow, 1954 (in Russian).
28. Chugaev, L. A., *Valency*, in book *New Ideas in Chemistry*, No. 3, St.-Petersburg, "Obrazovanie", 1913, p. 1-87 (in Russian).
29. Menshutkin, B. N., *Course in General (Inorganic) Chemistry*, Moscow, GIZ, 1924, p. 44, 45, 344, 345 et seq. (in Russian).
30. Kekulé, A., *Ann.*, 1857, Bd. 104, S. 129-150.
31. Butlerov, A. M., *Collected Works*, v. 1, Academy of Sciences Press, Moscow, 1953, p. 101-124 (in Russian).
32. Frankland, E., *J. Chem. Soc.*, 1866, v. 19, p. 377-378.
33. Friend, J. N., *The Theory of Valency*, 2 ed., London, 1915.
34. Kekulé, A., *Lehrbuch der organischen Chemie*, Bd. II, 1866, S. 257.
35. *Correspondance de Ch. Gerhardt*, v. I, Paris, 1918, p. 344.
36. Fayershtein, M. G., *Charles Gerhardt*, "Nauka", Moscow, 1968, p. 115 (in Russian).
37. Bykov, G. V., *The History of Classical Theory of Chemical Structure*, Academy of Sciences Press, Moscow, 1960, p. 33 (in Russian).
38. Kekulé, A., *Ann.*, 1858, Bd. 106, S. 129-159.
39. Odling, W., *J. Chem. Soc.*, 1854, v. 7, p. 1-22.
40. Brown, C., *The Theory of Chemical Combination*, Edinburg, 1861.
41. Frankland, E., *Lecture Notes for Chemical Students*, London, 1866.
42. Kekulé, A., *Z. Chem.*, 1867, [2], Bd. 3, S. 214-224.
43. Kekulé, A., *Ber.*, 1869, Bd. 2, S. 365-368.
44. Erlenmeyer, E., *Z. Chem.*, 1864, Bd. 7, S. 628-635.
45. Wurtz, A., *Cours de philosophie chimique*, Paris, 1864, p. 75.
46. Delavaud, Ch., *Bull. Soc. Chim.*, France, 1865, v. 4, p. 421-429.
47. Blomstrand, C., *Die Chemie der Jetztzeit*, Heidelberg, 1869, S. 397.
48. Fayershtein, M. G., *From the History of Natural Science*, Materials of 2nd Moldavian conference on history of science and technology, Oct. 1966, Academy of Sciences of Moldavia Press, 1966, p. 66-70 (in Russian).
49. Frankland, E., *J. Chem. Soc.*, 1866, v. 19, p. 378.
50. Sestini, F., *Nuovo Cimento*, 1871, Ser. 2, Tomo V-VI, p. 274-280.
51. Lossen, W., *Ann.*, 1880, Bd. 204, S. 288-292.
52. Claus, A., *Ber.*, 1881, Bd. 14, S. 432-435.
53. Markownikoff, V. V., *Selected Works*, Academy of Sciences Press, Moscow, 1955, p. 202 (in Russian).

*Chapter
Three*

Development of the Valency Concept in the Aspect of the Theory of Periodicity

The discovery of the periodic law by Mendeleev has produced a great effect on the development of many concepts in chemistry, the theory of valency included. It is in connection with this historical event in chemistry that it became possible to divide the entire history of the theory of valency into three periods. The first period, covering the 1850-1860s, is characterized by the emergence of the valency concept and its evolution in the framework of organic chemistry. The previous chapter of this book was dedicated to this period. The second period continued for over fifty years, from the early 1870s till the middle of the 1920s. It was characterized by the evolution of the valency concept in the light of the periodic law. And finally, the third period, the development of the theory of valency and periodicity within the framework of electronic, and mainly quantum-mechanical theories of structure of atoms and molecules, starting with the extension of quantum mechanics onto the field of chemism in 1926-1928 and till the present time.

There are no distinct boundary lines between these periods. Mendeleev approached the periodic law from the standpoints which dominated in views on valency in the 1850s and were not well defined, and he could not develop his theory of periodicity disregarding these views. The idea of periodicity, which appeared in the second period, continued developing in the time when the quantum-mechanical theory became a scientific principle in chemistry. The history of valency is divided into periods only by convention and the periods are not therefore equivalent in many respects. For example, the second period is characterized by special heterogeneity of concepts of valency. First of all, this period can be subdivided into two smaller periods: before and after the discovery of the electron. Secondly, a fruitful idea of partial valencies by Thiele appeared in the middle of this period which was a kind of a landmark in the evolution of the valency concept. Nevertheless the criterion of the second period is quite obvious—the all-embracing influence of the law of periodicity of properties of chemical elements.

1. Relationships Between Valency and Other Properties of Elements According to Mendeleev

As Kedrov [1] shows, Mendeleev was moving towards the discovery of the periodic law during fifteen years during which he systematically studied the four measurable properties of chemical elements and their compounds, *viz.*, isomorphism, the ratios of compound volumes, the composition of compounds, and the atomic mass ratios. When Mendeleev started on his famous "Principles of Chemistry" (1868), like many other chemists who studied inorganic compounds, he was influenced by the theory of types by Gerhardt [2]. And since this theory was directly connected with the concepts of valency they also influenced Mendeleev when he planned his future book.

It should be noted that the valency concepts had been used to classify chemical elements before the periodic law was discovered. For example, Meyer compiled a table in 1864 where all elements were arranged in six columns according to their valencies (ν):

ν	4	3	2	1	1	2
					Li	Be
	C	N	O	F	Na	Mg
	Si	P	S	Cl	K	Ca, etc.

When Mendeleev started his classification of chemical elements he also compiled such tables arranging elements in the order of their changing valencies in series of their oxides and halides:

	E_2O	EO	E_2O_3	EO_2
ν	1	2	3	4

In March 1869, Mendeleev finished his first version of "Experience with Systematization of Elements by Their Atomic Weights and Chemical Similarity" and wrote the paper "Relation of Properties to Atomic Weight of Elements" which was read by Menshutkin to the Russian Chemical Society (March 6 (18), 1869). This was the first report in press of the discovery of the periodic law. The report, along with the general formulation of the law ("Elements arranged in the order of their increasing atomic weight show vivid *periodicity* of properties"), read also the following: "comparison of elements or their groups by their atomic weights corresponds to the so-called atomicity and certain differences in their chemical character, which is obvious in the series Li, Be, B, C, N, O, F, and can be found to repeat in other series" [3].

It is important to note that at the first stage of his work, which gave the "Experience with Systematization of Elements", Mendeleev wanted to establish regularities in formation of compounds from elements of two types and, through these regularities, to reveal the most characteristic valencies of said elements. Therefore, like many his contemporaries, he chose the valency of 2 as the basic one for the 2nd group elements (elements of the insert decades). And it was for this reason that he described the elements of the modern decades "at magnesium" in his "Fundamentals of Chemistry". At the second stage of his work Mendeleev grouped together dissimilar elements by using other valencies of elements, i.e. he completely gave up the constant valency concept.

At the first stage of his work Mendeleev acted in the spirit of Dumas, i.e. compared changes in the atomic mass, atomic volume, and valency. But at the second stage he used isomorphism as the main property and compared it with valency. As a matter of fact, he derived a rule according to which isomorphism was regarded as a sign of similarity of only those elements which were present in the same state, i.e. had the same valency. Element-analogy in the system could be considered to exist only on the condition that isomorphic were the highest forms of compounds, e.g. KMnO_4 and KClO_4 , K_2CrO_4 and K_2SO_4 , $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 24\text{H}_2\text{O}$ and $\text{NH}_4\text{In}(\text{SO}_4)_2 \cdot 24\text{H}_2\text{O}$. The two former examples were important to establish the short form, while the latter, in the verification of the position of indium in the system. The isomorphism of $\text{MeSO}_4 \cdot 7\text{H}_2\text{O}$ vitriols does not indicate a higher likeness of elements, like in the previous case, and as Mendeleev compares them, he indicates only similarity of valency and hence of the general state of the element, i.e. the so-called "horizontal" similarity.

2. Valency and Relationships Between Forms of Compounds

By the term "form of compounds" Mendeleev understood certain quantitative and qualitative characteristics of a molecule which indicate that a given compound belongs to oxides, hydrides, acids, bases, or salts, and can be expressed by the formulas E_nO_m , EH_n , $\text{H}_n\text{E}_m\text{O}_p$, EOH , etc. Compounds belonging to one form thus are: (a) MgO , CaO , and BaO ; (b) KMnO_4 and KClO_4 , etc.

While creating his theory of periodicity, Mendeleev formulated and developed three rules which correlate different forms of compounds with valency of elements.

The first rule concerns the relationships between the forms of compounds with elements in their highest valency by hydrogen and oxy-

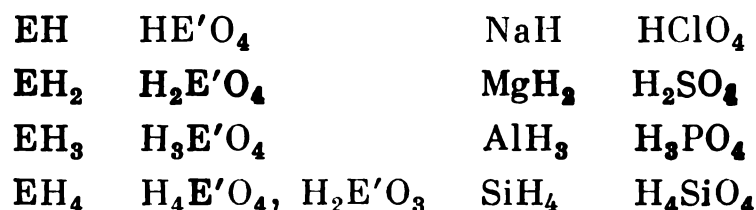
gen:



For example: CH_4 and CO_2 , SH_2 and SO_3 .

This rule is very important, for it substantiated the number of eight as a real base for the periodic law.

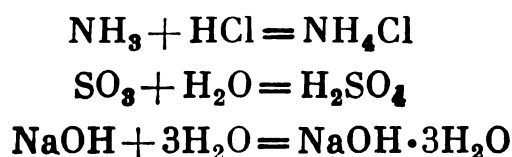
The second rule is about the relationships between the forms of hydrogen compounds and the highest existing oxyacids and about their regular changes in the horizontal series of the element-analogues:



or, in the general case, $EH_n - H_nE'O_4$.

This rule binds elements of lower and higher valency (1 and 7, 2 and 6) and also mean and mean (3 and 5, 4 and 4) valencies. The rule is interesting in that it shows the role of valency in the formation of the entire Periodic system of elements.

The third rule concerns the relationships between binary and molecular, or complex, compounds:



i.e. $EX_n + E'X_m = EX_{m+n}E'$.

The first rule is known best of all, the second rule was sometimes used, and the third rule has remained almost unknown.

3. Valency and Elements Position in the Periodic System

Soon after its emergence, the concept of valency was given different interpretations, and hence different assessment of its role among the other chemical concepts. This situation was characterized by Mendeleev as "uncertain". The previous chapter shows that chemists disputed the nature of valency and possible variation of its quantitative characteristics; they often confused this concept with the concept of chemical bond.

"A question naturally arises, writes Chugaev in his essay "Valency", whether or not the concept of valency loses its significance, its *raison d'être* in this situation" [4, p. 29]. And Chugaev believes that the history of chemistry gives a definite answer to this question: the concept of valency remains important and will not disappear

from the science. On the contrary, its favourable effect on the progress of chemistry will continue.

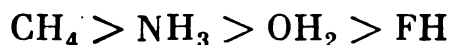
"There is another circumstance, writes Chugaev, that has strengthened the position of the theory of valency. This circumstance is the discovery of the periodic law" [4, p. 33]. But what effect did the discovery of the periodic law produce on the theory of valency?

The answer can be as detailed and comprehensive as exact and concrete. We shall try to formulate it in the form of several most important propositions, or rules, established in the 1870-1880s.

1. The periodic law establishes that the number of the group, to which a given chemical element belongs in the periodic system, is numerically equal to the valency of the element in its higher salt-giving oxide or, in other words, to its highest valency. For example, for the elements standing in the third series:

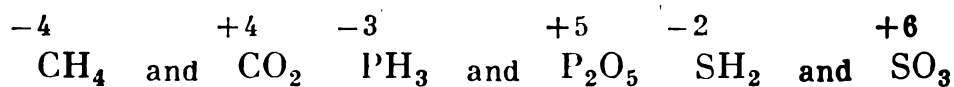
Group	I	II	III	IV	V	VI	VII
Oxide	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl ₂ O ₇

2. The valency of elements in their higher volatile hydrides regularly decreases from group IV to group VII:



This rule illustrates the different manifestation of valency in hydrides and oxides. Further it leads to the concept of two types of valency, *viz.*, valency by hydrogen and by oxygen, or positive and negative valencies, which in turn brings us to the concept of the electrical nature of "affinity" and chemical bond.

3. The sum of the highest valencies of elements by oxygen and hydrogen is equal to a constant value of 8. This rule agrees with the one mentioned in the previous section of this chapter:



4. The elements standing in the odd groups of the periodic system have mainly odd valencies:

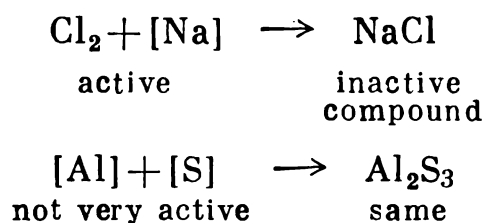
Group	I	III		V			VII		
Valency	1	1	3	3	5	1	3	5	7
Compounds	Na ₂ O	InCl	InCl ₃	PCl ₃	P ₂ O ₅	Cl ₂ O	KClO ₂	KClO ₃	KClO ₄

And on the contrary, even valencies dominate in the elements standing in the even groups of the system: II—2, IV—2 and 4, and in VI—2, 4, and 6.

5. The farther from one another stand elements in the periodic system, i.e. the greater their valencies by oxygen and hydrogen dif-

fer, the more stable compounds they form: LiF, NaCl, etc. are more stable than MgS, AlCl₃, etc.

6. The greater the difference in the valencies of elements by oxygen and hydrogen, the less chemically active are their compounds, and the greater the difference between the activity of these compounds and the activity of the starting simple bodies:



(Brackets indicate here the solid phase of the substance.)

All these rules were established soon after the discovery of the periodic law [4] and, along with the other regularities inherent in the theory of periodicity, they were the precursors of the electronic theories in chemistry.

Using these rules, the periodic law generalized the vast experience related to the theory of variable valency of elements to legalize, in a certain sense, the ideas of inconstancy of valency and of valence numbers variation in both oxygen compounds (e.g. N₂O, NO, N₂O₃, N₂O₄, N₂O₅) and hydrogen compounds (e.g. from N₂O₅ with N⁵ by oxygen, to NH₃ with N³ by hydrogen).

In the 1870s, new regularities in the variation of valency of elements depending on their position in the Periodic system were revealed. It became gradually evident that the parity rule does not equally hold for the elements of the odd series (*sp-elements*) and even series (now mainly *d-elements*): the elements of the main sub-groups of even groups give stable compounds with even valencies, and unstable with odd, while in odd groups the picture is reverse. It is known that this rule does not hold for the additional sub-groups. Mendeleev held to the same opinion. He considered the parity rule as an important regularity in inorganic chemistry.

In accordance with the idea of two types of elements (our main sub-groups and insert decades), which was formed short before the discovery of the periodic law and in the process of development of the idea of periodicity, several other rules were discovered which revealed the existence of two types of change in valency, depending on the position of the element in the system:

1. The parity rule holds for the main sub-groups and does not hold for the additional sub-groups.

2. Stability of the higher forms of compounds decreases in the elements of the main sub-groups and increases in the elements of the additional sub-groups in the downward direction (to be more exact, the Byron rule of the secondary periodicity holds here).

3. In compounds formed by elements of two different types but standing in one group of the system, the greatest similarity is observed in cases where the highest valency is attained: KClO_4 and KMnO_4 ; K_2SO_4 and K_2CrO_4 , etc.

4. Auto-oxidation-reduction reactions are typical of all compounds of the elements in the insert decades, especially during thermolysis in the solid and gaseous phases; these reactions for the elements of the main sub-groups become more characteristic with the increasing number of the group (*p*-elements).

5. The elements of the insert decades easier give the higher forms of compounds with oxygen (EO , E_2O_3 , EO_2 , E_2O_7 , EO_3 , E_2O_5 , EO_4) than with halogens and other elements.

A special stability of compounds having the composition 1 : 1 is observed in the series of elements of the main sub-groups (NaCl , MgS , LiF , BeO , etc.).

The systematization of the concepts of valency in the light of the classical (pre-electronic) theory of periodicity gave an impetus to new investigations in the essence of affinity, and the nature of chemical interaction. Among these investigations stands out a wonderful attempt by van't Hoff to explain, as if from the inside, through the nature of chemical action, the theory of valency on the whole [5]. And although van't Hoff's model of the atom and its valency potentialities is purely geometrical, his hypothesis foreshadowed many electronic concepts. Among these investigations are also fruitful theoretical works of Helmholtz, Thomson, and then Abegg, which lead to concepts of electric affinity, and of positive and negative valencies [6]. Important events in the development of the theory of valency are the studies in the field of chemistry of complex compounds, and first of all the deep reconstruction of this theory undertaken by Werner.

In the 1870-1890s with the development of theoretical chemistry and chemical synthesis, the concept of valency came into steady use in chemical research and literature, and it became necessary to work up methods for determining valency of various elements and for verifying already known valency numbers. Thus, in the 1870s, discussions took place at which valencies of beryllium, indium, yttrium, lead, gold, silver, platinum metals, cerium, and uranium were discussed. The discussions resulted from insufficient reliability of methods by which valency was determined, and another cause was the variation of valency numbers in one and the same element in its various compounds. The only reliable judge for the solution of disputable questions was the Periodic system of elements with its perfect criterion, the place which a chemical element occupies in the system.

In his book "Recent Theories in Chemistry", published in 1877, Meyer wrote that he did not consider it "right to determine atomicity

only from compounds which pass into the gaseous state without decomposition". He indicated that the law formulated by Mendeleev "and also the system of elements established by Mendeleev and myself, ... are a better ground for determination of atomicity than labile hydrogen and chlorine and the like compounds" [7].

In the 1970s nobody suspected of the force of this criterion: "place that an element occupies in the system". But this power could be felt in all coordinates used in the system, in the numbers of the groups, in their odd and even numbers, in the arrangement of subgroups, in numbers, and also odd and even numbers of the series, and finally the most important point — the number of the box occupied by the element. The "place of the element in the system" stimulated Mendeleev's verification and correction of already known atomic masses which however did not agree with the atomic masses calculated by Mendeleev for the boxes of the elements. The investigations showed that Mendeleev was right and that the atomic mass of indium is not 75.6 but 113.4 (to be more exact 114.82) and that of cerium not 92.0 but 138.0 (now 140.12).

But by the end of the past century it became clear that the position of an element in the Periodic system is determined not only by its atomic mass, but by the whole set of its chemical properties, which in turn show themselves in the valent potentialities of an atom. And early in the 20th century science went deeper into the mystery of the universal interdependence in nature: it established the relationships between the place of an element in the periodic system and the atom structure, i.e. the charge of its nucleus and the number of valency electrons. This explains the gradual growth of the importance of the valency theory in the systematization of elements.

4. Mendeleev's Attitude Towards Valency

The discovery of the periodic law gave a great impetus to the development of the valency theory which returned its action onto the development of the ideas of periodicity to highly stimulate the progress in this direction. Surprising as it may seem, but Mendeleev, the creator of the Periodic system of elements, was rather cool to the idea of valency.

Of course Mendeleev understood that his system "agrees with the atomicity in that form in which it is usually understood" [3, p. 33] but in his first paper, devoted to the discovery of the periodic law, he decisively gave up the idea of using valency for systematization of elements and did not acknowledge valency as a scientific concept.

"Many chemists in our days are inclined to the idea of distributing chemical elements by their *atomicity*, wrote Mendeleev. There is much uncertainty in the very principle underlying this tendency.

This theory arose from the study of organic compounds, organometallic compounds in particular, from applicability to them of the law of even shares, from the general concept of the limit of chemical compounds, and from the tendency to disregard the flexible theory of types. This approach is either inapplicable or only slightly applicable to compounds of other elements. For example, nitrogen and mercury form many odd share compounds. Such elements as vanadium, molybdenum and tungsten, manganese, chromium, uranium, arsenic, antimony and the elements of the platinum group form compounds of variable atomicity. These compounds are so specific and they so poorly agree with the concept which we get from the acquaintance with organic compounds, that it is impossible, at least at the present time, to apply the strict concept of atomicity to understanding of compounds of these elements" [3, p. 12]. Mendeleev also indicates that the formulas which are used for determining valency are quite varied and great in number. Furthermore, it is difficult to choose an element which could be assumed a standard of valency. Mendeleev writes that he doubts the use of oxygen as such a standard, since oxygen can be "pushed in between any two elements" [3, p. 13]*.

The critical attitude of Mendeleev towards the concept of valency persisted through years of his scientific work, beginning with 1861 when he published his textbook of organic chemistry where he wrote that "there is much of convention in the concept of atomicity" [8].

It is interesting to note that Mendeleev's attitude towards valency was quite peculiar. After the discovery of the periodic law the theory of valency became more substantiated and deeper in its meaning, and the number of its critics was reduced probably to Mendeleev alone. The cause of such a paradoxical phenomenon is peculiar too.

All Mendeleev's investigations were concentrated in the field of composition, within the limits of the first conceptual system in chemistry studying the qualitative conversion of substances and the relationships between the composition and the properties of substances [9]. Mendeleev opposed structural chemistry (the second conceptual system). He considered it as the theory of statistic of molecule construction, which, he thought, negated any dynamics. But the concept of valency arose from the investigations in structural organic chemistry. First it was regarded only as an invariable number of affinities inherent in an unlinked atom, as a certain abstraction in the theories of Kekulé and Butlerov. The number of affinities of a free atom was found to coincide (almost everywhere) with the num-

* Mendeleev means here the numerous interpretations of empirical formulas, such as e.g. Al_2O_3 , which can be written $\text{O}=\text{Al}-\text{O}-\text{Al}=\text{O}$ and $\text{Al}-\text{O}-\text{O}-\text{O}-\text{Al}$, the valency of oxygen being 2 in both.

ber of atom bonds in a molecule of organic compounds, and the original concept of valency was therefore extended to characteristics of a bound atom. It became one of the main concepts in practically all theories of structural chemistry.

Mendeleev did not recognize this "structural" role of valency. He understood it as a characteristic of an element which could be derived from the composition of a substance, from its empirical formula. But his interests were concentrated mainly in inorganic compounds (i.e. almost completely outside the field of investigations of structural chemistry) and the only use that he could get from valency of elements in inorganic compounds was to calculate it by the formula $v = (\text{atomic mass})/(\text{equivalent})$ using the composition of any substance, e.g. K_2O , CaO , FeO , Fe_2O_3 , Fe_3O_4 , SnCl_2 , SnCl_4 , etc. But such calculations inevitably convinced Mendeleev that valency varied, and neither the theory of composition nor structural (organic) chemistry of that time could explain the cause of such variations.

And still, why did other chemists see the importance of valency in chemistry, and Mendeleev did not? The answer to this straightforward question must be as straightforward too. Firstly, Mendeleev underestimated the role of structural chemistry in general. This was a disadvantage in his scientific work. And secondly, because he probably had a deep mental insight (perhaps much deeper compared with his contemporaries) into the essence of the object of inorganic chemistry. Long before the physical methods have proved that most inorganic compounds are not a simple combination of molecules of the type NaCl , ZrO , Fe_2O_3 , etc., but monocrystals of variable composition (kind of berthollides), Mendeleev understood it by intuition, and therefore by all possible means he tried to synthesize the stoichiometric concepts of Proust and Dalton with the ideas of Berthollet. And this is to the great credit of Mendeleev's scientific achievements.

But ... without trying to justify the former disadvantage of Mendeleev, we want to note that even if this genius of chemistry had been an active adept of the structural theories, then, while studying *inorganic* compounds by the methods and experimental techniques of his time, he *could not* have developed a *better* attitude to the concept of valency than he actually had. The experimental tools of his time could not help the investigator penetrate into the depth of chemistry of solids so that he could assess the positive and negative effects of the theory of atoms and molecules on the development of inorganic chemistry. But this theory was so much worshipped, that it was merely impossible to denounce a molecule as a Procrustean bed to which all oxides, hydrides, salts, and atomic crystals were artificially adapted. And this, of course, was an obstacle that hindered the development of inorganic chemistry.

References

1. Kedrov, B. M., *Discovery of the Periodic Law by Mendeleev*, in book by Kedrov and Trifonov, "Periodic Law and Chemical Elements", Nauka, Moscow, 1969 (in Russian).
2. Mendeleev, D. I., *Collected Works*, v. 13, Academy of Sciences Press, Moscow-Leningrad, 1949 (in Russian).
3. Mendeleev, D. I., *Periodic Law. Main Papers*, Academy of Sciences Press, Moscow, 1958, p. 30-31 (in Russian).
4. Chugaev, L. A., *Valency*, in book "New Ideas in Chemistry", No. 3, St.-Petersburg, "Obrazovanie", 1913, p. 1-87 (in Russian).
5. Van't Hoff, J. H., *Ansichten über organische Chemie*, Bd. 2, Brunswick, 1878-1881, cited from the Dictionary of Scientific Biography, Edit. Ch. Gillespie, v. XIII, N. Y., Ch. Scribns, 1975, p. 623.
6. Abegg, R., *Z. anorgan. Chemie*, 1904, Bd. 39, S. 330-380.
7. Meyer, L., *Die modernen Theorien der Chemie*, 1877, S. 6.
8. Mendeleev, D. I., *Organic Chemistry*, St.-Petersburg, 1861 (in Russian).
9. Kuznetsov, V. I., *Dialectics of Development of Chemistry*, Nauka, Moscow, 1973, p. 328 (in Russian).

Chapter Four The Theory of Valency and the Coordination Theory

1. Hypothesis of Constant Valency and Its Criticism

In 1891-1893 and later, the theory of valency was enriched with entirely new ideas from the coordination theory of Werner. For a better understanding of these propositions it is necessary to revive some basic stages in the history of development of the theory of valency.

In 1857, Kekulé stated that all chemical elements are characterized by *constant* valency.* Monovalent are H, Cl, Br, K; divalent O, S; trivalent N, P, As, and finally tetravalent, carbon [1, p. 132-133].

Couper also regarded valency as the most important property of an element which determines its character. But unlike Kekulé, Couper supposed that some elements, carbon and nitrogen included, can vary their valency [2].

The hot dispute around this valency problem continued for many years. Kekulé's hypothesis of constant valency was not supported by Butlerov, who in 1863 indicated that sulphur, probably, could be tetra- and hexavalent [3, p. 507]. In his textbook "Introduction to Complete Study of Organic Chemistry" (1864) Butlerov stated in detail his views of the theory of valency, and emphasized that elements can have variable valency. For example, carbon is tetravalent in carbon dioxide and divalent in carbon monoxide [4].

In 1864 the French scientist Naquet published his paper where he used such compounds as SCl_4 , SeCl_4 , TeBr_4 to prove that sulphur, selenium, and tellurium can be di- and tetravalent [5].

In the same year of 1864, Kekulé published his paper "Atomicity of Elements" [6] where he sharply criticized Naquet. According to Kekulé, valency is "the fundamental property of an atom, which is as constant and invariable as its atomic weight". If Naquet had been right, wrote Kekulé, then we had had to admit that nitrogen, phosphorus, and arsenic were pentavalent. But all these elements are known to be trivalent. According to Naquet, sulphur, selenium, and tellurium are tetravalent, while they are divalent.

Assuming sulphur to be divalent and nitrogen trivalent, Kekulé admitted that in nitric and sulphuric acids the atoms of oxygen can,

* See Chapter 2.

like carbon atoms in organic compounds, combine with each other to form chains. So he ascribed the following structure to nitric acid [7]: $\text{O}=\text{N}-\text{O}-\text{O}-\text{H}$. As to sulphuric acid, its constitution according to Kekulé is "with a great degree of certainty" $\text{H}-\text{O}-\text{S}-\text{O}-\text{O}-\text{O}-\text{H}$ [8].

Supporters of the constant valency tried many artificial methods to explain facts which contradicted their views. Bazarov noted sarcastically that "some chemists try to prove tetravalency of carbon in all its compounds by assuming that two affinities of carbon in CO saturate each other. But this means to be dipped in such a mist where all criticism becomes impossible" [9, p. 146].

The English scientist Newlands, in his attempt "to save" tetravalent carbon, suggested that carbon monoxide might be a dimer having the formula C_2O_2 . Two carbon atoms in a molecule of this

compound are interconnected by a double bond [10]:
$$\begin{array}{c} \text{C}=\text{O} \\ || \\ \text{C}=\text{O} \end{array}.$$

The constant valency concept did not explain the existence of many inorganic compounds such as ammonium chloride NH_4Cl , or phosphorus pentachloride PCl_5 . Kekulé found a way out: in 1864 he suggested that chemical compounds should be differentiated into "atomic" and "molecular" compounds [11]. Only atomic compounds consist of true molecules in which all elements are interconnected by mutually saturated affinities of their atoms. Atomic compounds are ammonia NH_3 , phosphorus trichloride PCl_3 , tellurium bromide TeBr_2 , etc. The specific characteristic of atomic compounds is their stability: only atomic compounds can pass into the gaseous state without decomposition.

As far as molecular compounds are concerned, the bond in them, according to Kekulé, is not accomplished between separate atoms but between chemically saturated, or "whole" molecules. The structure of such compounds cannot therefore be expressed by formulas in which the bond between atoms is shown. According to Kekulé, molecular compounds are formed as follows. Atoms, which are parts of molecules of various compounds, retain their power to attract each other. This attraction pulls the molecules together—the phenomenon which always precedes chemical decomposition. But it may happen (especially in cases where mutual decomposition is impossible because of the nature of the atoms themselves) that the reaction stops at the nearing stage, and two molecules then stick together (are "cemented") to form a group characterized by certain stability, which however is less than the stability of atomic compounds. This explains why molecular compounds do not pass into the vapour state on heating but fall into molecules from which they were formed. According to Kekulé, the internal "arrangement" of atoms remains unchanged in the "cemented" molecules. They preserve their own

characteristics during this "cementing" and are not bound by the valency forces acting between atoms.

Assuming that nitrogen and phosphorus have constant valency 3, Kekulé regarded, e.g. ammonium chloride as a molecular compound formed by "cementing" of NH_3 and HCl molecules, and the formula of ammonium chloride according to Kekulé is $\text{NH}_3, \text{HCl}^*$. Kekulé's formula for phosphorus pentachloride (molecular compound) is $\text{PCl}_3, \text{Cl}_2$. Tellurium tetrabromide is a molecular compound formed by "cementing" of TeBr_2 and Br_2 molecules ($\text{TeBr}_2, \text{Br}_2$). And finally, iodine trichloride is also a molecular compound, ICl, Cl_2 .

In all named molecular compounds, the component elements retain their constant valencies, viz., 3 in nitrogen and phosphorus, 2 in tellurium, and 1 in iodine.

Much data of inorganic chemistry, however, disagreed with Kekulé. According to Kekulé the nature of phosphorus pentachloride as a molecular compound is proved by that it does not exist in the vapour state and decomposes into PCl_3 and Cl_2 on heating. But phosphorus pentafluoride, the analogue to phosphorus pentachloride, passes into the vapour state without decomposition. Hence it cannot be referred to molecular compounds and should be regarded as an ordinary atomic compound. The classification of chemical compounds into atomic and molecular by their ability to pass into the vapour state without decomposition should, in the aspect of the history of chemistry, be assessed as "an artificially built border wall", which "would only add to the confusion of conceptions and produce many unsolvable contradictions" [12, p. 281].

Interesting ideas concerning valency and chemical affinity belong to Wurtz, who convincingly proved the insolvency of Kekulé's hypothesis of constant valency.

In 1864 Wurtz declared the following: "... From the law of multiple proportions we know that the capacity of elements to combine is exhausted gradually until it attains a maximum which cannot be passed over. This maximum combining power is called atomicity** by some authors; atomicity is invariable for each element because it is determined by the limit of saturation. But for me the term "atomicity" has a wider meaning. I am trying to determine the role played by each element in a given compound and ascribe it the combining power which it shows in this particular compound and not the combining power that it might show in some other compounds.

* Kekulé's suggestion that ammonium chloride was a molecular compound of the composition NH_3, HCl was especially bitterly criticized, because from the time of Berzelius scientists thought that ammonium salts, ammonium chloride in particular, contained monovalent radical NH_4 whose chemical behaviour was like that of alkali metal atoms [9, p. 146].

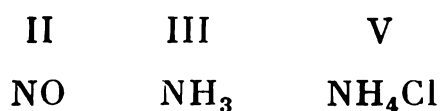
** The terms atomicity and valency are synonyms. In the 1850-1860s the term atomicity was in common use.

Can we definitely state that nitrogen is a triatomic element? If we do, then how shall we explain its role in ammonium chloride, where the sum of the elements connected with nitrogen is expressed by five units of chemical force.... Now the true meaning which we give to the concept of atomicity becomes clear. This concept expresses not only the potential and absolute combining power of a given element (or a group) but rather the factual combining power of an element which it displays in a given substance and which can be different in other substances" [13, p. 111]. Wurtz also noted that the term "combining power" is not quite correct because "it implies the idea of a potential power". In his opinion it would be better to define atomicity of an element as equivalency of its atoms, i.e. their "value" with respect to its ability to combine with or substitute for atoms of other elements [13, p. 112].

In Wurtz' opinion the power of affinity or chemical energy should be regarded as something relative, which depends on the nature of the element with which a given element reacts. For example, chlorine's power of affinity for hydrogen is rather high, while for oxygen it is small. This conclusion is confirmed by the fact that the affinity sometimes increases and sometimes decreases under the effect of physical factors such as heat, light, electricity. "Affinity is therefore a relative property, emphasized Wurtz; it is not absolute, like, for example, atomic weight" [14, p. 165].

Wurtz indicated that it is necessary to distinguish between affinity, i.e. the power which shows itself in the interaction between atoms, from the valency of an element, i.e. the power of its atom to combine with or substitute for a certain number of atoms of another element. He emphasized also that valency is as relative a property of atoms as is their affinity. The action of atoms is reciprocal, and the properties of one of them produce a certain effect on the properties of the other, so the atoms are a kind of adapted to one another. It is proved by the fact that such elements as nitrogen and phosphorus can form compounds with three atoms of hydrogen and with three atoms of chlorine; but phosphorus, in addition, can combine with five atoms of chlorine, while nitrogen can not. Thus he illustrated variation of valency in said elements as they combine with hydrogen and chlorine atoms.

Being an adherent of the variable valency concept, Wurtz indicated that nitrogen is divalent in nitric oxide, trivalent in ammonia, and pentavalent in ammonium chloride:



"Nitrogen can combine with three atoms of hydrogen, wrote Wurtz; it can substitute for three atoms of hydrogen in many organic com-

pounds; but it can also form a compound with four hydrogen atoms and one atom of chlorine" [13, p. 112].

Wurtz criticized Kekulé and his supporters, who regarded compounds of the NX_5 type as molecular compounds formed by two separate interconnected particles: $NX_5 = NX_3 + X_2$. "I could hardly imagine, wrote Wurtz, that a chemical compound ... could be formed by simple arrangement of particles relative one another ... and that these particles could retain some of their individual properties when united in such a compound" [14, p. 176-178]*. Wurtz indicated the insolvency of this view. He was convinced that "compounds in question (i.e. the compounds of the NX_5 type, — *Yu. S., P. S.*) are true chemical compounds which dissociate on heating" [14, p. 179].

At the same time Wurtz could not agree with some scientists who regarded ammonium chloride as an atomic compound. He had "a presentiment" that the structure of compounds similar to ammonium chloride is much more complicate than it seemed to many of his contemporaries. "Some authors assume, he wrote, that ammonium chloride NH_4Cl belongs to the NX_5 type compounds and conclude that the atom of chlorine and four atoms of hydrogen are connected each with the pentavalent nitrogen independently of each other. But can chlorine cancel its affinity for hydrogen in order to combine with nitrogen, which has a weak affinity for chlorine?... This discrepancy in the explanation of ammonium chloride structure disappears if we admit that in ammonium chloride the affinity of chlorine for hydrogen is saturated not by combination with the said hydrogen atom, but by the attraction which the chlorine atom produces on all hydrogen atoms into whose sphere it is placed in this case" [14, p. 179].

Further Wurtz explained the mechanism by which NH_3 can combine with HCl : "Ammonia can combine with hydrochloric acid because nitrogen atoms are so constructed, or better to say are given such motion, that they can admit into their system not only three atoms of hydrogen but also its fourth atom and one atom of chlorine, and furthermore, because the motions of these five atoms can be coordinated with the motion of the nitrogen atom into a new system of known form and known attraction in space.... The ability of an atom comprised in ammonia to combine with a particle of hydrochloric acid is regarded as a common substantial property" [14, p. 180-181].

Discussing the nature of ammonium chloride, Wurtz suggested that when ammonia combines with hydrochloric acid "a new equi-

* It should be noted that earlier (1864) Wurtz admitted the existence of molecular compounds. For example, he supposed that "amylene hydrate", an isomer of amyl alcohol, was a molecular compound of an unsaturated hydrocarbon with water [15, p. 132].

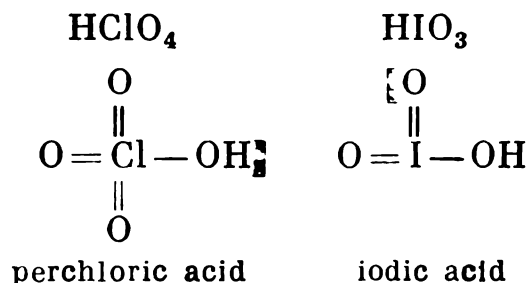
librium state between all elements is established where mutual attractions *radiate* between the atoms of nitrogen, chlorine, and hydrogen. Such is the play of the affinity force, i.e. the chemical energy, here" [14, p. 180].

Wurtz wanted to establish the structure of ammonium chloride, but, as we shall further see, it was Werner, the author of the coordination theory, who did it.

Trying to disprove Kekulé's suggestion that valency is constant, Wurtz gave many examples that vividly proved the insolvency of this standpoint. He showed that iodine is monovalent in ICl and tervalent in ICl_3 , while carbon is divalent in CO and tetravalent in CO_2 .

In 1864, Wurtz arrived at a conclusion that "atomicity of an element varies depending on a particular compound into which it enters" [13, p. 110]. At the same time Wurtz thought that chlorine had constant valency. He assumed that chlorine remains monovalent in oxygen compounds, i.e. shows the same valency as in compounds with hydrogen and metals. According to Wurtz, oxygen atoms in chlorine compounds are connected with each other to form chains. Each oxygen atom combines with the neighbouring oxygen atom to lose one "affinity unit, so that only the extreme atoms of oxygen still have a free affinity unit which is saturated with chlorine" [13, p. 113]. Wurtz' formula of chloric anhydride Cl_2O_7 is $\text{Cl}-\text{O}-\text{O}-\text{O}-\text{O}-\text{O}-\text{O}-\text{O}-\text{Cl}$.

The structure of oxygen compounds of halogens was studied by the German chemist Kaemmerer in 1869. He criticized Wurtz' formulas with his oxygen chains. He indicated that "oxygen compounds of the halogens are difficult to describe with rational formulas, which is obvious from Wurtz' formulas, unless we admit that the halogens themselves are polyatomic" [16, p. 414]. In Kaemmerer's article the structural formulas of oxyacids of halogens do not differ from the formulas which we use now, e.g.



At the end of his article, Kaemmerer wrote: "I think that this assumption (polyvalency of halogens, — *Yu. S., P. S.*) is unreasonably objected and regarded as "arbitrary". But in fact, this suggestion, as well as the entire theory of atomicity, is only the expression of indisputable facts" [16, p. 414].

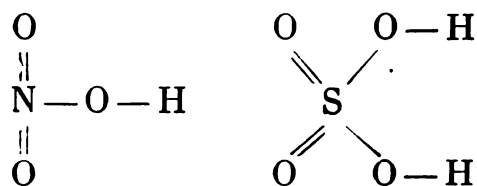
In 1869, the Swedish chemist Blomstrand joined the adherents of the variable valency concept. "There were many debates around

the question whether the property of being saturated is constant or it is variable and depends on the conditions under which saturation takes place.... At the very first sight we can get convinced that atomicity is constant only in rare cases, first of all in oxygen, hydrogen, and fluorine. Our experience shows that atomicity varies within strictly definite and rather narrow limits" [17, p. 102].

Blomstrand also indicated that the maximum valency of chlorine is seven, and that in some compounds the valency of sulphur is six. At the same time, both chlorine and sulphur with their analogues form compounds in which their valency is lower. Moreover, their valency can be both odd and even. For example, in oxygen compounds chlorine can be mono-, ter-, penta- and heptavalent [17, p. 186].

"Variable ability to saturation, emphasized Blomstrand, is the main property of an atom" [17, p. 187]. But the Swedish chemist, like all his contemporaries, could not predict the maximum valency for a given element. He correctly indicated that when sulphur acts like an electronegative element (i.e. in compounds with hydrogen and metals) it is undoubtedly divalent, while in oxygen compounds it is, also undoubtedly, tetra- and hexavalent. But can the valency of sulphur be higher than six? The Swedish scientist admitted that there may be an oxygen compound of sulphur where it is octavalent (SO_4).

Blomstrand was the first to give correct structural formulas of such oxygen-containing acids as nitric and sulphuric acids. He proposed so-called "centred" formulas for these compounds, in which the central place is occupied by a non-metal, while oxygen atoms or hydroxyl groups are arranged around this centre and interconnected by valency units. Blomstrand's formulas for nitric and sulphuric acids were as follows:



Bazarov indicated that Blomstrand had revived the half-forgotten Berzelius' concepts of the electrochemical character of elements, and emphasized that "electrochemical relations ... will, probably, occupy an important place in theoretical chemistry". To Bazarov it was clear at that time (1870s) that the "so-called electrochemical character of elements produces an indisputable effect on atomicity. The atomicity which an element displays towards positive elements is often different from its atomicity towards negative ones" [9, p. 154].

Thus Bazarov indicated that the halogens are monovalent with respect to electropositive hydrogen, and polyvalent towards electronegative oxygen. In this connection he criticized Wurtz for his monovalent chlorine in oxygen compounds and chain-like formulas. "Oxygen compounds of halogens, wrote Bazarov, are a clear evidence that chlorine, bromine, and iodine can be 3-, 5-, and 7-valent.... It is impossible to assume that the bond between several oxygen atoms is the same as that between carbon atoms in organic compounds, because ... judging from the inconstancy of ozone (O_3) ... oxygen cannot be compacted as carbon in all its compounds, this ability of carbon to be compacted being important for the properties of carbon even in the elementary state" [9, p. 152]. Bazarov made the following general conclusion: "The concept of variable atomicity is nothing but a direct conclusion from facts" [9, p. 148].

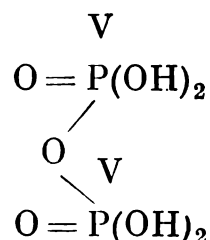
A few years later Wurtz recognized that his former views on the structure of oxygen compounds of chlorine were wrong. "I thought that in some chlorine compounds rich in oxygen, he wrote, chlorine atoms could be connected to form a chain. So I expressed the structure of chloric and perchloric acids as follows: $Cl-O-O-O-H$ and $Cl-O-O-O-O-H$ But this suggestion was disproved and I had to reject my former hypothesis concerning the structure of these acids. It would be difficult to explain the existence of oxygen chains in highest acids of chlorine in view of the increasing stability of these compounds, which grows with the number of oxygen atoms. I adhere now to the opinion that chlorine is heptavalent in perchloric acid.... Admitting that atomicity can gradually change we have also to admit that atomicity of a given element towards oxygen can be seven times higher than towards hydrogen" [14, p. 168].

Wurtz was right to indicate that in some cases, namely in hydrogen peroxide and its derivatives, we must admit the existence of two interconnected oxygen atoms. He gives the structural formulas of hydrogen peroxide and barium peroxide:



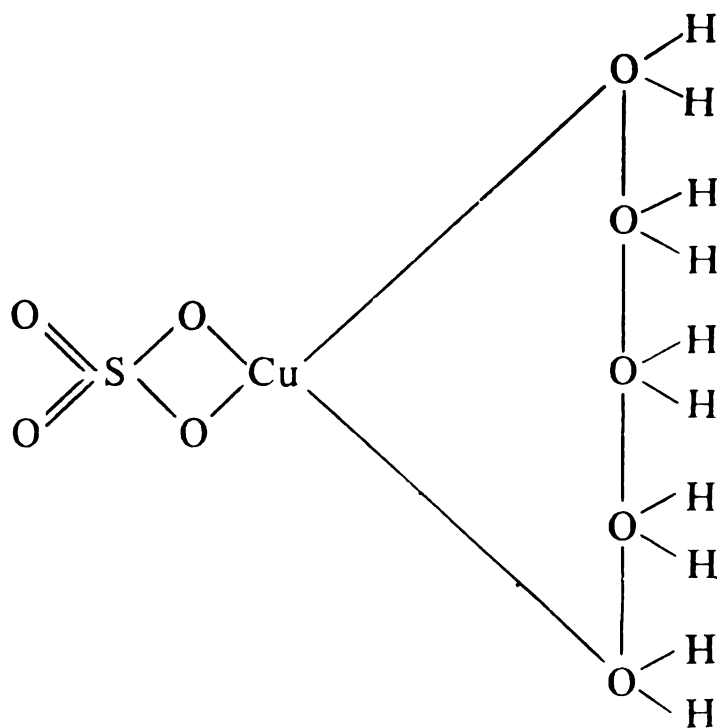
Considering the problem of valency of iron in pyrite, FeS_2 , Wurtz, in 1864, indicated that iron is not necessarily tetravalent in this compound, since we do not know other compounds where iron had the same valency. He justly suggested that two sulphur atoms in pyrite can be "soldered together" like two oxygen atoms are interconnected in peroxides. It follows therefore that each sulphur atom uses one valency unit to be connected with the other sulphur atom and the group $[S-S]$ can therefore saturate only two valencies of iron in pyrite [13, p. 114].

In the 1870s Wurtz described the structure of some inorganic compounds, e.g. pyrophosphoric acid, as we do it now:



Wurtz attached great importance to structural formulas and emphasized that “the object of chemistry is to discover the structure of bodies, to determine the arrangement and the mutual position of atoms, and hence to determine the attitude of each atom towards its neighbour.... The properties of bodies are the function of their structure” [14, p. 172].

Wurtz rejected Kekulé’s idea of “atomic” and “molecular” compounds, and considered double salts and crystal hydrates as “ordinary” (“atomic”) compounds. He tried to show how atoms of different elements are interconnected in such compounds. For example, according to Wurtz, the structure of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is as follows:



It can be seen from this formula that Wurtz had to ascribe the unusual valency of four to oxygen and copper. So his attempt to explain the structure of crystal hydrates and double salts was a failure.

Meyer attached great importance to the problem of valency. In his book “Latest Theories in Chemistry and Their Importance for Chemical Statics” [18] he criticized Kekulé’s adherence to constant valency of all chemical elements. Meyer indicated that, e.g.

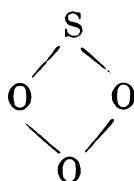
nitrogen and its homologues, which were regarded by Kekulé only tervalent, can in fact form "quite characteristic compounds" showing in them "their five-fold power of saturation". He referred compounds of the ammonium chloride type to this group: NH_4Cl , PH_4Br , PH_4I , and also halogen compounds, PCl_5 , PBr_5 , SbCl_5 [18, p. 60].

But Meyer did not ignore the fact that the compounds in which nitrogen and its homologues are pentavalent are usually unstable: they readily decompose on heating to give substances in which the valency of said elements is three. This led him to the idea that "affinity units" might be unequal. "It is possible to admit that nitrogen and its homologues, he wrote, in addition to three *strong* affinities, have also two *weak* affinities (italicized by Yu. S., P. S.), which can bind the fourth and the fifth atoms of a particle in a solid state, and sometimes even in a liquid state, but which are insufficiently strong to keep these two atoms when the particles of the substance are given so strong a motion in the form of heat that the substance passes into the gaseous state. We have to admit therefore that the increased heat motion disjoins not only whole particles, but can also separate two atoms (which are less strongly bonded) from a separate particle. But once we admitted it for nitrogen and its homologues, we shall immediately have to admit the existence of such weak affinities for the other elements" [18, p. 74].

Meyer indicated that in some compounds the halogens "have many affinities", e.g. iodine has three affinities in iodine trichloride ICl_3 . But of the three, only one is a strong affinity unit, whereas the other two are weak. This is proved by the fact that ICl_3 decomposes on heating: two chlorine atoms bonded by weak affinities are eliminated to form ICl , in which iodine still has one strong affinity unit.

"The number of such examples is great, wrote Meyer. But even our examples vividly show that we have certain grounds to admit the existence of weak affinities" [18, p. 76].

Admitting that many elements had variable valency, Meyer thought at the same time that sulphur and its analogues in all compounds, oxygen compounds included, have the constant valency of two. The structure of sulphur trioxide, according to Meyer, could be described by the following formula [18, p. 53]:



In the 1870s Meyer gave up his former views to declare that sulphur and its analogues are divalent only in compounds with electropositive elements, whereas their valency in oxygen compounds is four or six. In his special note Meyer indicated that Butlerov

had been the first to indicate that sulphur could be hexavalent [19, p.] 273].

Like Kekulé, Meyer recognized the existence of molecular compounds but in his opinion they were only complicate inorganic substances, such as crystal hydrates and double salts, e.g. double chlorides, $K_2PtCl_6 = 2KCl + PtCl_4$, and double cyanides, e.g. potassium ferrocyanide, $K_4Fe(CN)_6 = 4KCN + Fe(CN)_2$, and potassium ferricyanide, $K_3Fe(CN)_6 = 3KCN + Fe(CN)_3$. "There are very many cases where particles which we must consider as having no free affinities, nevertheless, do combine together," wrote Meyer.

Meyer gave his own description of the formation of molecular compounds. In his opinion, in order to explain their existence it is not at all necessary to "condescend to affinities of separate atoms". He emphasized that molecular compounds are not formed "as true chemical compounds" where each atom can bind a definite and limited number of other atoms.

He explained the formation of molecular compounds by mutual attraction of chemically saturated "particles" (molecules). He supposed that the "sum of all attractions which the atoms in a given particle produce onto the atoms of another particle can be sufficiently strong to keep both particles in the state of mutual attraction, that is to form a kind of chemical combination of particles". In Meyer's opinion, various molecular compounds (crystal hydrates, double salts, and others) are formed "by one and the same kind of action" [18, p. 79].

2. Valency Problem from the Aspect of Mendeleev's Periodic Law

The valency problem appeared in a new light after the discovery of the periodic law in 1869. Mendeleev indicated that with his discovery, valency (atomicity), along with the atomic mass, had become an important characteristic of a chemical element. "Today, to characterize an element, he wrote in 1871, it is also necessary to know its atomic weight and atomicity. The law of periodicity, which explains the interdependence of these two functions, makes it possible to determine one of them, namely the so-called atomicity, from the other, i.e. atomic weight; the periodic law therefore determines also the forms of chemical compounds of an element" [20, p. 147].

The discovered periodic dependence of the properties of elements, valency included, on their atomic weights, disproved Kekulé's idea of constant valency. Mendeleev convincingly proved that valency of a given non-metallic element in hydrogen compounds differs from its valency in oxygen compounds. The numerical value of

both valencies is determined by the position of the element in the Periodic system. Mendeleev indicated that valency varies in the elements of the 5th and the 6th groups: "The elements of the 5th group give RH_3 and R_2O_5 , i.e. their atoms are 3-atomic towards hydrogen, and 5-atomic towards oxygen. The elements of the 6th group are diatomic towards hydrogen and 6-atomic towards oxygen, etc." [20, p. 167].

The disadvantage of all former concepts was the impossibility of predicting the maximum valency. And only "the law of periodicity indicates the limit of oxygen combining power, to remove... a serious disadvantage of the theory of atomicity of elements" [20, p. 165].

In Mendeleev's opinion, the theory of valency had a "serious disadvantage" which consisted in that it "had much conventional" and did not disclose the inner state which atoms assume in various compounds, the valency being the same (e.g. Fe_2O_3 and FeCl_3).

Mendeleev sharply opposed Kekulé on molecular compounds. He considered that the classification of chemical compounds into atomic and molecular was the attempt to save the subjective idea of constant valency. "It is evident that there is something artificial in the concept of molecular compounds, wrote Mendeleev, and this is the result of the dominating theory of a strongly limited combining abilities of elements" [21, p. 1024].

Speaking about Kekulé's characteristics of molecular compounds as compounds incapable of passing into the vapour state, Mendeleev noted that "this definition cannot stand the slightest criticism" [22]. He repeatedly indicated that "it is unlawful to separate molecular compounds from atomic ones, first of all because the strength of a compound is quite variable and there is no sharp boundary line between stable and unstable compounds" [21, p. 1024]. Dwelling on the same question in his "Fundamentals of Chemistry" (1871) Mendeleev wrote: "The boundary line which is artificially drawn between molecular and atomic compounds makes harm to the correct development of science" [23, p. 842].

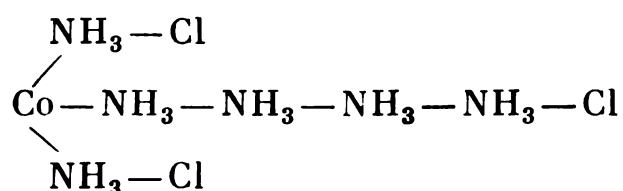
So, according to Mendeleev, all inorganic compounds are "atomic" in their nature, i.e. they are composed of elements whose atoms are bonded with one another.

3. "Residual Affinity" of Atoms

In the 1870s Mendeleev studied the structure of complicate but still "atomic" compounds, such as crystal hydrates, ammoniates ("ammoniated metal" salts), and double salts.

We know that Wurtz tried to explain the structure of crystal hydrates but his suggestion that oxygen and metal (copper) are tetravalent in these compounds was unrealistic.

Blomstrand and Jörgensen, who believed that nitrogen had variable valency and could be not only ter- but also pentavalent, arrived at a conclusion that the nitrogen atoms of ammoniates, like carbon atoms in organic compounds, are capable of combining with each other to form chains of various lengths. The links of these chains are ammonia molecules ($\text{—NH}_3\text{—NH}_3\text{—}$), just like methylene radicals ($\text{—CH}_2\text{—CH}_2\text{—}$) are the links in the chains of organic compounds. According to the “chain” theory of Blomstrand-Jörgensen, the structure of hexammine cobalt chloride (luteo-salt) was represented as follows:



The “chain” theory was criticized in 1871 in the “Fundamentals of Chemistry” by Mendeleev. He studied in detail the properties of platinum ammoniates and arrived at the conclusion that “the special properties of ammonium and platinum changed” in these compounds. Mendeleev explained it by “their mutual combination”, whereas Blomstrand and Jörgensen believed that the molecules of ammonia in the ammoniates were bound not only with the metal but also between themselves to form chains. Mendeleev rejected this idea and indicated that “it is hardly possible” to admit the bond of nitrogen with platinum and nitrogen in such stable compounds as ammoniates, “because these affinities are very weak and cannot account for the strength of these compounds; we should rather expect explosive, unstable substances” [24, p. 719]. Mendeleev indicated that as platinum combines with ammonia these two substances “do not undergo their usual reactions any longer”, and hence a question: “How do the elements contained in such compounds (ammoniates) relate to each other?” A thorough study of the properties of platinum ammoniates led Mendeleev to the conclusion that the atom of platinum is in the centre of their molecules, and this atom is connected simultaneously with the acid residue and the molecules of ammonia. In this connection he suggested an idea of valent potentialities of atoms which show themselves in the formation of compounds such as ammoniates and double salts. For example, the PtX_4 type compound is the limit of halogen compounds of platinum, but the tetravalent platinum in PtCl_4 can still form double salts. In Mendeleev’s opinion this certainly indicates “the presence in platinum of PtCl_4 of certain residual affinities which are responsible for the formation of new, more complicate, forms from the platinum compounds of the PtX_4 type” [23, p. 839].

Similar ideas can be found in all editions of Mendeleev's "Fundamentals of Chemistry". For example, in the fifth edition of this book, which was published in 1889, he wrote: "After all, we see that platinum has not only four affinities, which show in PtCl_4 , but we admit that it can have them in greater quantity" [24, p. 720].

Further developing his views Mendeleev arrived at an important conclusion concerning "residual affinities" of atoms. This is what he wrote in this connection: "The forces by which such a considerable number of ammonia particles are retained at a particle of cobalt compounds belong to that kind of only slightly studied residual affinities, which exist even in higher compounds of most elements. These are the same forces which form compounds with water of crystallization, double salts" [24, p. 701].

The idea of residual affinity was developed by the English chemist Pickering. In his article "Theory of Residual Chemical Affinity as Explanation of Physical Nature of Solutions" (1891) [25] he suggested that molecules of "simple" ("atomic") compounds have a certain ability of saturation or, in other words, have "residual affinity" by which they can be bound with other molecules. "I am inclined to consider residual affinity, Pickering wrote, as a result of incomplete saturation of the affinity which is inherent in the combining atoms. The suggestion of the existence of residual affinity is based on the opinion that affinity units, which are inherent in atoms, are, to a certain degree, divisible" [25, p. 3632-3633].

Residual affinities show themselves in that molecules of a solvent are symmetrically grouped about the solute molecule, which acts as a certain centre.

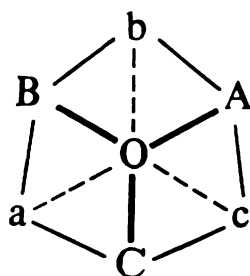
In Pickering's opinion these forces of residual affinity are responsible for the formation of such complicate inorganic compounds as double salts. He regarded residual affinities of molecules of "simple" compounds as their residual electrical charges which are due to residual electric charges of the combined atoms.

Similar ideas were developed in 1895 by the English scientist Armstrong [26]. He thought that when two atoms combine with each other, their charges are neutralized incompletely and the formed molecules have therefore a certain residual charge, or affinity. Hence they can interact with other molecules. For example, water, in Armstrong's opinion, is an unsaturated substance; its oxygen atom has residual affinity. Sulphuric acid is not saturated either. Water and sulphuric acid can therefore combine with each other to form hydrates. Like Mendeleev, Armstrong thought that residual affinity is of the same nature as the ordinary one, the difference between them being non-qualitative rather than qualitative in character [26].

4. Spatial Concepts and the Theory of Chemical Affinity and Valency

Meyer's idea of inequivalence of affinity units was given a spatial interpretation in original ideas of the German scientist Michaelis. He declared that unlike gravitational forces, chemical affinity (attraction of atoms) is not uniform in all directions: its tension is higher in some directions and lower in others [27]. As a result, an atom of a given element can securely unite only with a definite number of atoms of other elements, this number depending on the direction of the strongest attraction. As to the atoms which are attached by the action of chemical affinity in the direction of lower attraction, they are united much weaker in the molecule.

Using Michaelis' idea, van't Hoff, in 1884, tried to explain variable valency of chemical elements as follows: "It is quite clear that the deviation of the atom configuration from that of a sphere must result in that the attraction in known directions, namely in the directions by which a given atom can approach the other atoms to a minimum distance, will be stronger than in the other directions. We shall thus have a certain number of directions of the maximum action or, in other words, a certain number of affinity units, or valency" [28]. To explain himself, van't Hoff gave a picture of an atom in the form of an irregular hexagon



In this model we can see three directions of the maximum attraction (OA, OB, OC) and three directions of the "secondary" importance (Oa, Ob, Oc). This model can function either like a hexa- or like a tervalent one, depending on the surroundings and the physical conditions of the reaction, first of all on temperature.

Stereochemical concepts produced a peculiar effect on some chemists. For example, Lossen wrote: "We, chemists, are now waiting that we shall be clearly told what a unit of affinity actually is, since we already can picture its position in space" [29, p. 340].

In 1886, Wunderlich, in his work "Configuration of Organic Molecules" emphasized that "matter of an atom is not concentrated in one single point but is distributed over its various parts the sum of which makes up the volume of the atom" [cited from 30, p. 35].

The surface of atoms has special sites, so-called "sites of attachment" whose number is equal to the valency of a given element. An atom of element A can be saturated by an atom of element B only if the "sites of attachment" of both approach each other to a very close distance, so close that it is insignificant as compared with the size of the atoms. If by some reason the "sites of attachment" of two combining atoms of elements A and B are not so close to each other, the atoms will not be fully saturated.

Wunderlich supposed that the atoms of both elements are united by the attraction force which acts between the sites of attachment of given atoms; the force of attraction depends on specific affinity of the combining atoms and on the distance between the attachment sites [cited from 30, p. 37].

In his article "On Position of Atoms in Space" Wislicenus, in 1888, considered atoms as complicate spatial trimeric formations. "I think that atoms can most likely be compared with complex radicals and that, like radicals, atoms have certain sites where 'affinity units' are located and from where they act" [31, p. 584].

The problem of distribution of affinities inside an atom was discussed by many scientists. In this connection Wislicenus wrote: "I don't think it is improbable that the carbon atom might be a formation whose configuration is more or less... like a regular tetrahedron.... The causes of those actions which factually show themselves as affinities are concentrated in the vertices of this tetrahedral formation" [31, p. 584].

Wislicenus suggested interesting ideas on the complexity of the structure of atoms which, in his opinion, consist of smaller particles, which he called "protoatoms". These protoatoms are the actual carriers of the "specifically chemical form of potential energy", like chemical energy of complex radicals is "undoubtedly the resultant of the energies inherent in elementary atoms" [31, p. 584].

In Wislicenus' opinion, the study of configuration of molecules will help understand the form of elementary atoms and will give information on spatial distribution of their spheres of action, known as affinity units.

To end the discussion of the evolution of the valency theory before Werner, we shall give a concise outline of the views of Lossen and Claus whom the creator of the coordination theory considered his direct predecessors.

In his paper "On Distribution of Atoms in a Molecule" (1880) [29] Lossen characterized valency as the value indicating how many other atoms are present in the zone of binding of a given atom. Valency of an atom can be expressed by a whole number, but it is a variable value. Constant is only the maximum valency which indicates the maximum number of other atoms which can be located inside the "binding zone" of a given atom.

Lossen supposed that valency depends on two factors, *viz.*, on the overall affinity forces of the combining atoms and on the possibility of contact between their "binding zones".

Claus in the paper entitled "On the Problem of the Magnitude of Affinity of Carbon" (1881) resolutely rejected the idea that a carbon atom might have constantly inherent four units of affinity, or, using his terminology, "units of attraction", which act separately and are characterized by equal numerical values. It was Claus' conviction that the hypothesis of pre-existence in polyvalent atoms of "units of attraction" of definite strength is groundless and "unnatural". "I can rather imagine, he wrote, that chemical force of attraction, inherent in the so-called polyvalent elementary atom, is a whole unit, which, when a given atom enters into a chemical compound with other atoms, can be split into a different, but limited, number of parts, which may be equal or unequal, depending on the other atoms which combine with the given atom" [32, p. 433].

5. Werner's Model of Carbon Atom

Lossen's and Claus' ideas were further developed by Werner in his paper "To the Problem of Theory of Affinity and Valency" (1891) [33] where he considered important theoretical problems using organic chemistry data for his conclusions.

Werner maintained that "affinity is the force of attraction acting from the centre of the atom uniformly towards all parts of its spherical surface" [33, p. 133]. Assuming "for the sake of simplicity" the atom to be of spherical shape, he considered it as a "certain spatial part of universal matter".

As an atom is bound with some other atom, it loses part of its affinity which corresponds to a certain circular site on its spherical surface. This site was called by Werner "bonding surface", while the points where two spherical atoms come in contact, "valency sites". Werner suggested that as a given atom forms a chemical bond with other atoms, part of its spherical surface is covered ("consumed"), and the other part remains free. The number of circular sites, which are formed on the spherical surface, depends on the number of atoms which are bonded with it, the size of the circles indicating the strength of the bond. Bonds are the strongest where the bonding surfaces are maximum, and do not overlap each other. Free parts of the spherical surfaces determine the "residual affinity".

Unlike Claus, Werner developed the model of a carbon atom. He suggested that, in compounds of the CR_4 type, the valency sites of R (radical) are located at the vertices of a regular tetrahedron, but only on the condition that all R are identical. If different radicals are united with the carbon atom, their binding

surfaces will be unequal, whereas the valency sites will be located at the vertices of an irregular tetrahedron.

Werner emphasized that the consumption of affinity for the construction of the simple C—C bond, and the strength of such a bond, cannot be equal in all compounds because of the mutual effects of the atoms. How did Werner explain the effect that the atoms, connected with the two carbon atoms, produce on the strength of the simple C—C bond? In his opinion this effect consists in quantitative redistribution of affinity (bonding surfaces) which was inherent in each of the two carbon atoms during formation of the C—C bond. This conclusion, which proceeds from new Werner's concepts of chemical affinity, is one of the most important conclusions for structural chemistry [34, p. 149].

Based on his theoretical concepts of chemical affinity, Werner indicated the cause of differences in simple bonds, which are however designated by the same symbol in structural formulas. In his paper "On Variations in the Simple Bond Value" (1906) Werner wrote that the "force" of a separate valency of each atom is not constant, but differs in various compounds depending on the other atoms or radicals that are bound with the same atom. "A simple valency dash, emphasized Werner, means quite different values of affinity" [35, p. 1278].

Werner's ideas of chemical affinity played an important role in substantiation of the coordination theory.

6. Coordination Theory of Werner

In 1893 an important event took place in coordination theory. A German journal of inorganic chemistry published Werner's article "On the Structure of Inorganic Compounds" [36] where he postulated his coordination theory, which opened a new era in the development of theoretical concepts of the nature and structure of complicated compounds such as crystal hydrates, ammoniates, and double salts, which, in 1889, were given a common name of complex compounds.

The role of the coordination theory in the development of inorganic chemistry is as important as that of the theory of chemical structure in the development of organic chemistry.

Like Blomstrand and Mendeleev, Werner disproved Kekulé's views on molecular compounds as groups of "cemented whole" molecules in which the inner "arrangement" of the atoms is retained. Werner believed that in complicated inorganic compounds, such as complex compounds, the chemical bond is accomplished between the atoms of elements. He chose the following quotation from Blomstrand as an epigraph to his book "New Concepts in Inorganic Chemistry" (1905): the main object of modern chemistry

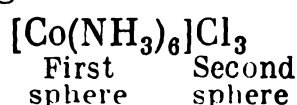
is "atomistic explanation of compounds, which were formerly considered with a greater or lesser degree of certainty as molecular, in other words, the explanation based on the ability of elements to saturation" [37].

According to the coordination theory, in the centre of a molecule of a complex compound located is an atom of an element (mainly metal) which acts as a complexing agent. It attracts (coordinates) atoms, atom groupings, and molecules characterized by chemical stability. All these particles were later given the name of ligands. So, these are only ligands that are bound with the central atom by direct bonds in a molecule of a complex compound. By its electrochemical nature the direct bond is non-ionogenic and therefore ligands are not eliminated in the form of ions in an aqueous medium; to be more exact, the elimination is insignificant.

Atoms and atom groupings characterized by chemical mobility are at a significant distance from the central atom and are therefore connected with it through an indirect bond which is of ionogenic character. Atoms and atom groupings, remoted from the central atom, are eliminated in the form of ions in an aqueous medium. For example, a molecule of the luteo-salt $\text{CoCl}_3 \cdot 6\text{NH}_3$ contains an atom of tervalent cobalt as the central atom, which is connected by a direct non-ionogenic bond with closely connected six molecules of ammonia, whereas three mobile (reactive) acid residues Cl , which are remoted from the central atom, are connected with it by indirect ionogenic bond.

In the light of the coordination theory, a molecule of a complex compound is a micro-world, resembling the macro-world, i.e. the Copernican (heliocentric) system. In the centre of the micro-world there is the central (complexing) atom, round which "planets-satellites", i.e. atoms, atom groupings, and molecules, are arranged at various distances from the centre.

In accordance with his hypothesis of the structure of complex compounds, Werner held that molecules of these compounds consist as a rule of two spheres, *viz.*, the first (inner) and the second (outer). The first sphere comprises the central atom and the ligands, directly connected with it. The second sphere comprises groups which are remoted from the central atom and bonded with it by indirect bond. "If we imagine a metal atom as a sphere, wrote Werner, then, together with ... groups directly connected with it, it forms a complex radical located in the first sphere, whereas the remaining groups are in the second sphere" [36, p. 323]. In accordance with his views Werner used new coordination formulas to describe complex compounds. For example, hexammine cobalt chloride had the following formula



Werner introduced into chemistry a new concept of the coordination number, which he defined as follows: "The number of atom groupings with which the elementary atom is coordinated into a complex radical can be given the name *coordination number*. If the coordination number of an atom is six, it can be bound directly with six groups, or, in other words, it can be coordinated into a complex radical with six groups" [36, p. 326]*.

Some elements, such as cobalt, iridium, or rhodium, have constant coordination numbers. But in some elements the coordination number is variable. The coordination numbers of 3, 4, and 6 are known for zinc.

Werner regarded the central atom** as a certain clot of matter which occupies a certain volume in space and upon which mainly depends the number of ligands that can be arranged round the coordinating centre. "We shall adhere mainly to the following, he wrote; each atom is a material point having a certain volume; the immediate surroundings are therefore limited and can hold only a definite number of atom groupings" [38, p. 392]. It follows therefore that the coordination number depends on the spatial relationships between the central atom and the ligands. Werner emphasized that the coordination number is a "spatial number".

It should be noted that long before Werner (in 1869), Blomstrand wrote that the limited number of particles which can be attached to a given atom depends on its volume: "If the atom can be characterized by a certain volume, then, at a certain moment of time, the sphere of action of the atom, which combines with other atoms, will be all filled" [17, p. 398].

The volume of the central atom (complexing agent) depends on its valency state. The coordination number of one and the same metal can therefore vary depending on its valency state. For example, the coordination number of tetravalent platinum is six, and that of divalent, four. It follows that when we indicate the coordination number of a metal characterized by variable valency, we must specify the valency which the metal shows in this particular case. When we state that the coordination number of copper is three, we must indicate that we mean monovalent copper, since the maximum coordination number of divalent copper is six in some compounds.

* As has been said earlier, Werner, in 1891, suggested an original idea that "affinity is a force of attraction acting from the centre of the atom uniformly towards all parts of its spherical surface". This idea is a theoretical precursor of the coordination number.

** By the term "central atom" is understood the atom in the ionized state, and not an electrically neutral metal atom. But the properties of such an ionized atom are not identical to those of the corresponding free ion, because its electron shell is deformed by the action of ligands attached to it.

But in some cases the volumes of ions of various valency in a given metal do not strongly differ and their coordination numbers are therefore equal. An illustration is di- and tervalent ions of iron: the coordination number of both is six.

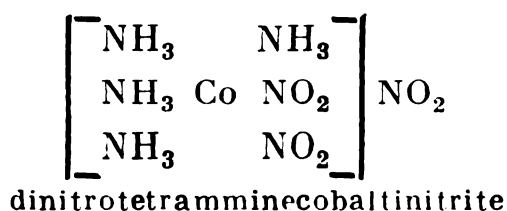
Werner characterizes the difference between the coordination number and the valency number as follows: "The valency number is the maximum number of monovalent atoms which can directly unite with the given atom *without participation of other elementary atoms*. The coordination number indicates the maximum number of atoms and groupings which can be bound directly with the given atom" [36, p. 328].

Werner attached a great importance to the coordination number in establishing the structure of complex compounds. "The coordination number, he wrote, in the theory of structure of complex compounds, which are formed by combination of various simple molecules, is as important as the valency number in the theory of structure of simple compounds, carbon compounds in particular" [36, p. 329]. Werner emphasized that the new concept which he introduced into chemistry, i.e. the coordination number, is the foundation of the theory of structure of inorganic compounds, just like the valency theory is the foundation for the theory of structure of organic compounds.

Werner compared the coordination and valency numbers of many elementary atoms. They proved to be different in all cases. There was only one exception, the carbon atom. Its coordination number is four and, as Werner indicated, "numerous examples of carbon compounds show that the maximum number of atoms or atom groupings which can be coordinated with the carbon atom is four. This indicates that the coordination number of carbon is four" [36, p. 327]. In Werner's opinion, "this accidental coincidence of the numerical characteristics of carbon might have delayed the differentiation of the two concepts" [36, p. 327].

As has already been said, according to Werner, the central atom (the complexing agent), together with ligands, forms the first, or inner, coordination sphere. For example, in the ammoniate $\text{Co}(\text{NO}_2)_3 \cdot 4\text{NH}_3$, the first sphere consists of the central atom Co and the ligands (which are connected with it), i.e. four molecules NH_3 and two acid residues NO_2 . As to the third acid residue, NO_2 , it is in the second, outer sphere, where it is connected with the central atom by an indirect ionogenic bond.

According to Werner the structure of $\text{Co}(\text{NO}_2)_3 \cdot 4\text{NH}_3$ is:



Only the acid residue contained in the second sphere can be eliminated in an aqueous medium in the form of the anion NO_2^- .

The acid residue NO_2 , which is located in the second sphere, is, in Werner's opinion, connected with the central atom, although this bond is indirect and should be understood in the "valency-chemical sense". Trying to explain the mechanism of this indirect bond, Werner suggested an original idea. He regarded the molecules NH_3 , H_2O , and others, which are directly bound with the central atom, as means of transportation of the central atom affinity force from the first sphere into the second one.

To illustrate his idea of the transportation of the affinity force of the central atom from the first sphere to the second one, which is remoted from it, Werner proposed the following electrostatic model: "Let us imagine a metal atom in the form of a sphere bearing a positive electric charge and surrounded by a neutral coat of water molecules. Then negative electricity will be accumulated on the inner surface of the neutral coat, while the positive electricity will accumulate on the outer surface. The outer surface of the coat will thus act by the same amount of positive electricity as the metal atom proper. If the coat is not absolutely neutral but is, for example, weakly positive, this will result in the corresponding increase in the amount of positive electricity acting in the direction of the second sphere. It is possible to suggest that likewise act molecules... of ammonia: they transport affinity to the sphere located far from the metal atom" [36, p. 324-325].

Werner did not insist that his model was a correct expression of the true mechanism of the indirect bond between the central metal atom and the atom groupings (acid residues) in the second, outer, sphere. He only used his model to show that the transport of the affinity force is possible in the physical aspect.

7. Main and Auxiliary Valencies

Werner indicated in his article in 1895 [38] that the existing theory of valency was inapplicable to complex compounds. In his opinion, it was necessary to give up the idea that the formation of complicate molecules of complex compounds can be explained only on the basis of valency numbers. Analysing the literature and using his own experience, Werner came to a very important conclusion: "*Even in those cases where it is possible to conclude, from the valency numbers, that the combining power of given elements is exhausted, these atoms in many cases are still capable of participating in further construction of complex molecules to give quite definite atomic compounds*" [38, p. 390].

Werner's aim was to further develop and to extend the theory of valency. He did it in 1902, when he published a comprehensive

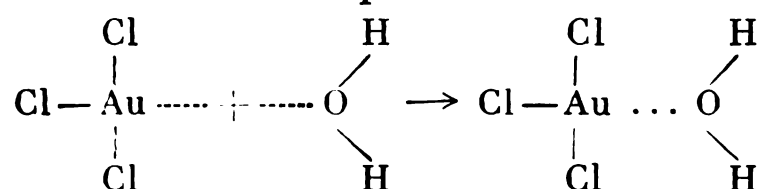
work [39] where he developed the ideas connected with the theory of valency. Werner proceeded from the fact that the so-called compounds of the first order (of the type SO_3 , H_2O , AuCl_3 , KCl , PtCl_4 , etc.) are not completely saturated, since the atoms contained in these compounds possess free affinities by which the independently existing molecules of the compounds of the first order can combine with each other to give compounds of the higher order, *viz.*, complex compounds. "Establishing coordination formulas for complex compounds, wrote Werner, leads us to the idea of the existence of new binding forces in many elementary atoms" [39, p. 268].

These new additional forces of elementary atoms, which show themselves in the formation of complex compounds, were given the name of the forces of auxiliary valency (to differentiate them, according to Werner, from the forces of the main valency which are responsible for the atom bonding in molecules of the first order compounds). The main valency is the ordinary valency and it can be determined by the number of atoms of hydrogen or some other monovalent elements which can be combined with a given atom. "Further I shall allude to the main valency, Werner wrote, in the sense of our ordinary valencies" [39, p. 268]. Thus, the valencies which show themselves, for example, in an atom of sulphur in SO_3 , or an atom of gold in AuCl_3 , are the main valencies.

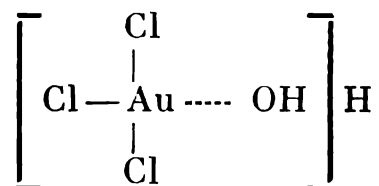
But, despite the fact that sulphur atoms in sulphur trioxide and gold atoms in auric chloride have shown their maximum ordinary valencies, they still have certain unused affinities in store. "The cause... of the ability of atoms to further combination is that, in addition to their main valency forces, they have forces of auxiliary valency" [37].

The sulphur atom in sulphur trioxide, the oxygen atom in water, the gold atom in auric chloride, the platinum atom in platinum chloride, etc. have forces of auxiliary valency which can be used to form complex compounds by combining molecules of the first order compounds. It follows that complex compounds are formed by mutual saturation of auxiliary valencies.

To illustrate Werner's ideas, consider the formation of the compound of a higher order (complex compound), auric chloride $\text{AuCl}_3 \cdot \text{H}_2\text{O}$, from compounds of the first order, *viz.*, auric chloride and water. The gold atom in a molecule of auric chloride and the oxygen atom of water have one auxiliary valency each. These auxiliary valent forces are mutually saturated to give a compound of a higher order, auric chloride. Using a broken line to show auxiliary valencies, we can describe this process as follows:

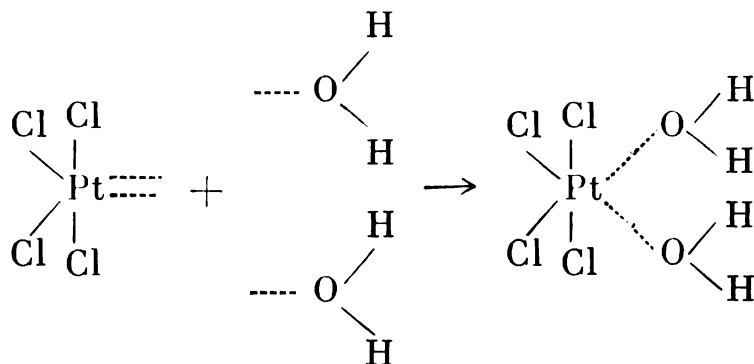


Since the hydrate of auric chloride is a monobasic acid, it can be represented by the following coordination formula:

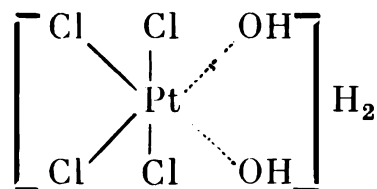


A molecule of another compound of the first order, platinum chloride, PtCl_4 , is capable of combining with two molecules of water to form the hydrate $\text{PtCl}_4 \cdot 2\text{H}_2\text{O}$. The platinum atom has therefore two auxiliary valencies. Like the main valency indicates the number of *monovalent atoms or atom groupings*, which can combine with the given element, the number expressing the auxiliary valency, wrote Werner, is determined by the number of *molecules* which can combine with its atom [37].

The mechanism of formation of platinum chloride according to Werner is as follows:



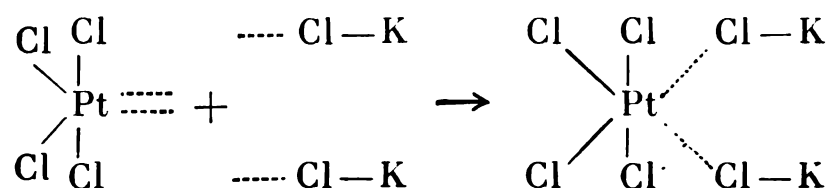
The hydrate of platinum chloride, $\text{PtCl}_4 \cdot 2\text{H}_2\text{O}$, is a dibasic acid, whose structure can be expressed by the following coordination formula:



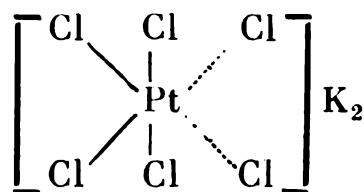
While discussing the problem of relationships between the forces of the main and auxiliary valencies, Werner wrote: "...One might expect that the forces of the main and auxiliary valencies differ in their essence; in fact, the forces of the main valency unite separate atoms into molecules of compounds of the first order, whereas the forces of the auxiliary valency, although associated with separate atoms, are applied to the atoms which have already been combined in molecules capable of independent existence. The forces of the main valency arise from $-\text{Cl}$, $-\text{Na}$, $-\text{NO}_2$, $-\text{CH}_3$, etc., and the forces of the auxiliary valency from $---\text{OH}_2$, $---\text{NH}_3$, $---\text{ClK}$, etc. But all attempts to draw a distinct line between the forces of the main and the auxiliary valency proved a failure. As

the time passes by, it becomes evident that sub-division of the valency forces into main and auxiliary is only a subsidiary and temporary measure, without which we cannot do at the present, transient, stage of the theory of valency. But in fact the forces of the main and auxiliary valencies are quite similar and may be even identical" [37, p. 66].

Werner's idea of possible identity of the forces of the main and auxiliary valencies is proved by the existence of the complex compound potassium chloroplatinate which is formed by the combination of platinum chloride PtCl_4 with potassium chloride KCl :

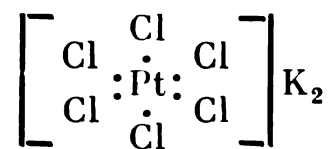


Since potassium chloroplatinate dissociates in water into the complex anion $[\text{PtCl}_6]^{2-}$ and potassium cations K^+ , Werner represented the structure of this salt by the following coordination formula:



In the starting substances, the compounds of the first order PtCl_4 and KCl , the acid residues strongly differ from each other by their properties: the bond is non-ionogenic in platinum chloride and ionogenic in potassium chloride. But as they form the complex compound potassium chloroplatinate, the properties of the acid residues are levelled and they all become non-ionogenic. Thus, all acid residues, no matter whether they are connected with the central atom by the main or the auxiliary valency, are characterized by similar chemical behaviour.

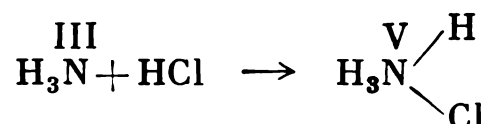
Since the properties of ligands connected by the forces of the main and auxiliary valencies are identical, Pfeiffer suggested that both valencies should be designated by dots in coordination formulas, for example:



Complete equivalence of ligands connected by the main and auxiliary valencies was proved in our days. It was done during the study of potassium bromoplatinate $\text{K}_2[\text{PtBr}_6]$ with radioactive indicators [40].

As we have already mentioned, Werner discovered the structure of ammonium salts using his coordination theory.

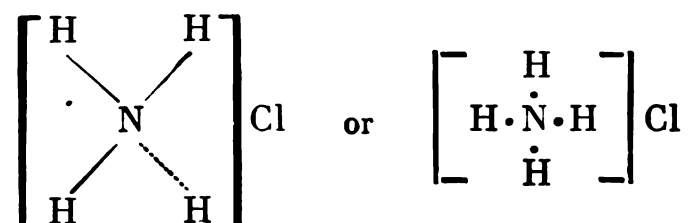
Supporters of the variable valency concept supposed that valency of nitrogen increases during formation of ammonium salts from three to five [39, p. 277]:



Werner resolutely objected the idea that ammonium salts are derivatives of pentavalent nitrogen. "In contrast to the commonly accepted opinion, Werner wrote, I adhere to the opinion that negative residues in ammonium compounds are not directly bound with nitrogen" [38, p. 417]. In his opinion, the nitrogen atom in the ammonia molecule has one auxiliary valency "in store". As ammonia reacts with hydrochloric acid this auxiliary valency is saturated by the auxiliary valency of the hydrogen atom contained in the molecule of HCl [39, p. 277]:



The formed ammonium salt is a complex compound in which all four atoms of hydrogen are ligands: they are directly bound with the nitrogen atom acting as the central atom, i.e. the complexing agent. Hydrogen atoms are connected with the central atom by equal amounts of affinity no matter whether they are connected with it by the main or the auxiliary valency. According to Werner, four hydrogen atoms still have certain amounts of affinities and the attachment of the acid residue Cl, located in the outer sphere, becomes therefore possible. The structure of ammonium chloride can be described by the following coordination formula:



"The degree of nitrogen saturation in ammonium compounds, emphasized Werner, differs from that in ammonia only by the participation of one auxiliary valency" [41].

Attachment of ammonia to hydrochloric acid does not change the character of the bond of the acid residue Cl: it remains ionogenic. In aqueous solutions of HCl and NH_4Cl , the acid residue is in the form of the chloride anion Cl^- .

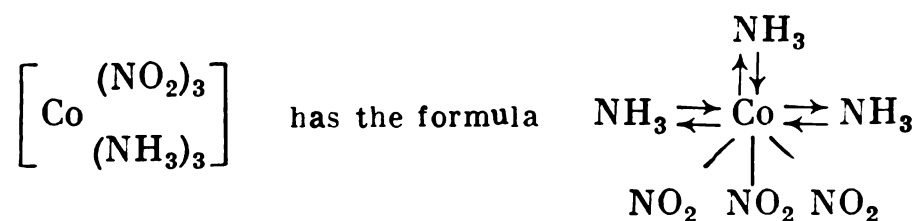
In Werner's opinion, only the coordination formula of ammonium salts explains their properties and agrees with the experimental data.

At the time when Werner announced his theory of the main and auxiliary valencies, the electron made its first steps on the triumphant road in chemistry. Werner was among the first who used the electron theory to explain the nature of the valency forces. "The main valencies, he wrote, are those whose ability to saturation can be measured owing to their equivalence with electron.... The auxiliary valency is a combining power sufficient to bind two atom groupings by the atomic bond, but insufficient to bind an electron" [39, p. 269].

In his article "The Theory of Valency" [42] Werner formulated the most important idea of "electron affinity". "Elementary atoms, he indicated, show the ability to bind electrons. So we must ascribe them affinity for electrons. The force of electron binding increases with growing electronegativity of the elementary atom" [42, p. 603]. Werner especially emphasized the dependence of the ability of elements to form ions on their atomic volume.

8. Electronic Theories of the Structure of Complex Compounds

As a vast experimental material was accumulated, it became necessary to explain the nature of the forces acting between ligands and the central atom, the complexing agent. The first attempt to solve this problem can be found in the work by Ramsay (1908). In his opinion the structure of complex compounds is as follows:



In this particular case Ramsay used J. Thomson's concept of "vector valency" (1907). According to Ramsay, coordination bonds are accomplished through two Faraday power tubes in opposite directions, while the ordinary, ionizing bonds through one tube. Three molecules of ammonia, connected directly with the atom of cobalt, each take one electron from the atom of cobalt and simultaneously return one electron of their own. This method Ramsay described by arrows to indicate the direction of electron transfer [43].

According to Lodge and Frankland (1904), a full bunch of force lines corresponds to the chemical "bond" or "affinity unit". The atom charge is indivisible, it is a kind of unit. But the power lines, which it emits, can be scattered to unite molecules into complex aggregations.

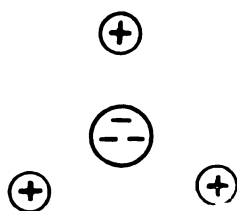
Developing Lodge's idea, Frankland gives the following picture of electrolytic dissociation of sodium chloride in an aqueous solution. In a dry salt, the atom of sodium is connected with the atom of chlorine by a Faraday bunch. As water acts on the salt, some threads in the bunch deviate to unite the atoms of sodium and chlorine with a molecule of water. If sufficient water is present, most positive lines deviate to destroy the bond between sodium and chlorine. This is the essence of the ionization phenomenon. The bond between hydrogen and oxygen in water weakens only insignificantly because only insignificant part of the power lines emitted from the atom of chlorine or sodium is directed to each molecule of water.

The first more or less successful attempt to explain the nature of the main and the auxiliary valency from the standpoints of the electron concepts belongs to Kossel. In 1916, he suggested an electrostatic model of a complex ion, whose stability he associated with the charge and the size of the central ion [44]. Kossel explained heteropolar chemical bonds by the electron transfer from electropositive atoms to electronegative atoms with formation of especially stable electron configurations, similar to those of inert gas atoms (stable, eight-electron outer shell).

Kossel indicated in 1928 that "it was Werner who made a suggestion, which however was not commonly accepted at that time, that the concept of separate directed forces of valency does not hold for many inorganic compounds, and that the power field of the atom should be regarded as entirely isotropic. This view perfectly agrees with our theory, according to which we deal with forms similar to those of noble gases. And even the most orthodox theory of separate directional forces cannot apply its principle of directional forces to noble gases" [46].

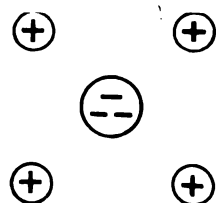
The coordination theory by Werner did not explain the coordination of neutral molecules, e.g. molecules of ammonia, round the metal ion, the complexing agent.

According to Kossel [46] the molecule of ammonia consists of a triply charged negative ion of nitrogen and three positively charged hydrogen ions which surround it. Schematically this structure can be shown as this:



According to Kossel, the triply charged negative ion of nitrogen can also unite with the fourth hydrogen ion (H^+). This is because the attraction of the triply charged nitrogen ion is stronger than the

repulsion of the three positively charged hydrogen ions. As a result, a group is formed, which is a singly charged complex cation



$[\text{NH}_4]^+$ which attracts the negative acid residue (anion) into the outer sphere of the ammonium salt, e.g. $[\text{NH}_4]^+\text{Cl}^-$.

As ammonium salts dissolve in water, the bond between the cation $[\text{NH}_4]^+$ and the anion $[\text{Cl}]^-$ breaks, whereas the bond between the central nitrogen ion and the surrounding ions of hydrogen is preserved. This, in Kossel's opinion, is explained by the high charge on and a small volume of the negative nitrogen ion (N^{3-}) which fastly holds all four positive hydrogen ions (H^+) and repels the anion of the acid residue (Cl^-). The arrangement of the four hydrogen ions at the vertices of the tetrahedron is, in ammonium salts, the result of their mutual repulsion.

Late in the 1920s, it became clear that molecules such as NH_3 and H_2O are electrically non-symmetrical. The electronegative part of the dipole molecule of ammonia is at the side of the nitrogen atom. By this part, the ammonia molecule is pulled into the field of the corresponding complexing agent. Thus the cause of coordination of neutral molecules round the metal ion, the complexing agent, was disclosed.

The theory of Kossel is the theory of heteropolar compounds. The central ion of metal is the main builder of complex compounds. The higher the charge on the ion, and the lesser its radius, the stronger the bond between the central ion and the ligands. Kossel and Magnus [47] helped reveal the physical essence of the coordination number and the nature of auxiliary valency which depends on the interaction of the electrical field of the complexing agent and the dipole molecules of the ligands.

The theory by Kossel was thus the first attempt to explain the physical nature of the coordination bond. It was far from the correct interpretation of the problem. Its vivid heteropolar character came in conflict with a "tougher" character of the coordination compounds. For example, it was not clear, why some ions, although they had equal charges and radii, behaved differently in the formation of complex compounds. Experimental data indicated that, in addition to heteropolar bond, some other forces, for which the theory by Kossel does not account, take part in the formation of complex compounds.

In 1936, Grinberg wrote in this connection that "in the majority of concrete cases, we deal with intermediate forms of bond. Of course,

we are right when we approach each chemical compound ... from both "heteropolar" and "homopolar" side. The truth is somewhere in the middle. It is like a little island in the middle of a marsh. We can reach the island either by electrostatic bridges or by wave-mechanical gangway, but both are still quite imperfect and we cannot feel safe on the island" [40].

Many papers published in the 1920s were dedicated to the elaboration of the electrostatic model of the structure of complex compounds. The detailed study made clear the role of the ionic radii, the structure of the outer electron shells of the central ion and the ligand ions (molecules) (Magnus, 1922; Fajans, 1924-1925).

In 1927-1928 Fajans studied the role of the polarization effects in complex formation processes [48]. Early in the 1930s, Van-Arkel, de Boer, and Nekrasov developed Kossel and Fajans' ideas and offered a new electrostatic model of complexes in which the main role is played by the charge and the size of the central ion, the charge, dipole moments, polarizability and the size of the ligand [49]. It was established that the higher the energy of polarization of the interacting ions, the stronger are they bound in a complex compound.

The electrostatic theory explained satisfactorily the existence of such complexes as $[\text{CuCl}_4]^{2-}$, $[\text{CuF}_6]^{4-}$, and others, but did not explain the stability of complexes with non-polar ligands of the CO, PF_3 type, and also the different stability of complexes formed by two central ions having equal charge and radius, e.g. Fe(III) and Co(III).

The polarization concept could describe qualitatively the mutual effect of the complexing agent (the central ion) and the ligands on each other, but it did not account for some conditions (e.g. the possibility of formation of a molecular orbital from two atomic orbitals) imposed by the quantum theory.

In the middle of the 1930s, a theory of crystal field arose from quantum mechanics. According to this theory, ligands are point charges, or dipoles, and in their field, the energy levels of the central atom undergo specific cleavage which depends on the geometry of the complex. Day and Selbin write in their book "Theoretical Inorganic Chemistry", which went out in the USA in 1969 in the second significantly revised and enlarged edition [50], that the importance of the theory of crystal field consists probably in that despite being rather artificial, it comparatively simply explains theoretically quantitative relationships between empirical and semiempirical values.... Its main disadvantage is probably the tentativeness of the theory which accounts only for the orbitals of the metal atom without consideration of the electronic structure of the ligands. Therefore, all properties depending on the orbitals of the ligand atom, their changes and interactions with the orbitals of the metal

atom cannot be regarded from the standpoints of the theory of crystal field. Day and Selbin also indicate that the tentativeness of the theory of crystal field is due to negligence of the covalency effects. The theory must be improved.

The electrostatic theory completely rejected the covalent character of bond and suggested that the bond between the ions of metal and ligand is fully ionic. The opinion of Sidgwick (1923) is different. He developed Lewis' ideas and understood that the coordination bond is covalent in its nature [51, 52].

Proceeding from the complicate structure of the atom, Lewis, in 1916, developed a theory of valency which was based on two main propositions. The first one is that each atomic nucleus tends to be surrounded with a closed electron shell similar to that of a noble gas. The second proposition is that two electrons belonging to different atoms form a homopolar (covalent) bond [53].

In 1923, the Faraday Society in London organized a general discussion on the electron theory of valency. In his report on the nature of the non-polar bond, Sidgwick said that his only new suggestion is that the orbit of each shared electron contains both attached nuclei [52]. During the discussion, one participant made an interesting suggestion that the bonding orbits might assume the shape of the figure eight.

According to Sidgwick, in the coordination bond, both electrons are taken from one of the components; the donating component is designated L and the accepting, M ($M \leftarrow L$)*. Sidgwick produced an idea of the effective atomic number, according to which the total number of electrons which are present round the complexing agent, including the electrons that are used for coordination, is equal to the atomic number of the corresponding inert gas, in other words, a complex compound is characterized by the formation of a stable electron configuration of the noble gas type.

The theory by Sidgwick explained the structure of some complexes (carbonyls, nitrosyls), but it could not account for the stability of other complex compounds.

Early in the 1930s, Pauling [54], based on the theory of covalent bond, made a suggestion which had to explain the cause and the mechanism of coordination, and also the magnitude of the coordination number and the geometrical configuration of the complex. According to Pauling, the mechanism of coordination depends mainly on the structure of the electron shell of the central atom. The coor-

* The arrow indicates the dative bond; it shows that the donor group (L) gives both electrons for the bond with the acceptor (M).

dination bond arises from the overlapping of the vacant orbital of the metal atom with the filled orbitals of the donating group.

The concepts of the coordination bond based on the theory of covalent bond were later developed in the 1950s in the theory of ligand field [55, 56].

The modern data obtained with EPR and NMR method indicate that markedly covalent bonds can exist, while purely ionic bonds do not exist. Unpaired electron can be delocalized even in such ligands as fluoride ions, which might be expected to form the most ionic bonds.

The theory of molecular orbitals was first applied to complex ions by Van Vleck in 1935 [57, 58].

The theory of molecular orbitals is at the present time the strongest one. It comprises the electrostatic theory as the limiting case, and can account for any degree of covalency and the π -bond [59].

We can make a general conclusion that the coordination bond is different from the "classical" chemical bond. The variety of coordination compounds is explained by the complicate combination of covalent, donor-acceptor, and dative bonds of various multiplicity and various delocalization.

References

1. Kekulé, A., *Ann. Chem. Pharm.*, 1857, Bd. 104, H. 2, S. 129-150.
2. Couper, A. S., *Ann. Chim. Phys.*, 1958, [3], v. 53, p. 469-489.
3. Butlerov, A., *Z. Chem. Pharm.*, 1863, Bd. 6, S. 500-534 (in Russian).
4. Butlerov, A. M., *Collected Works*, v. II, Academy of Sciences Press, Moscow, 1953 (in Russian).
5. Naquet, A., *Comp. rend.*, 1864, v. 58, p. 381-383.
6. Kekulé, A., *Comp. rend.*, 1864, v. 58, p. 510-514.
7. Kekulé, A., *Lehrbuch der organischen Chemie*, Bd. 1, Erlangen, 1859.
8. Bykov, G. V., *August Kekulé*, Nauka, Moscow, 1964 (in Russian).
9. Bazarov, A., *Journal of Russian physico-chemical society*, 1873, issue 4, vol. 5, p. 144-174 (in Russian).
10. *Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften*, Giessen, 1868.
11. Anschütz, R., *August Kekulé*, Bd. II, Berlin, 1929.
12. Meyer, E., *Geschichte der Chemie von den Ältesten Zeiten bis zur Gegenwart*, Auflage 3, Leipzig, 1905.
13. Wurtz, A., *Lectures on Some Problems of Theoretical Chemistry*, St.-Petersburg, 1865.
14. Wurtz, A., *La theorie atomique*, Paris, 1898.
15. Bykov, G. V., *The History of Classical Theory of Chemical Structure*, Academy of Sciences Press, Moscow, 1960 (in Russian).
16. Kaemmerer, H., *Ann. phys. Chem.*, 1869, [5], Bd. 138, S. 390-417.
17. Blomstrand, C. W., *Die Chemie der Jetztzeit von Standpunkte der electrochemischen Auffassung aus Berzelius Lehre entwickelt*, Heidelberg, 1869.

18. Meyer, L., *Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Statik*, Breslau, 1864.
19. Meyer, L., *Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Statik*, Auflage 3, Breslau, 1876.
20. Mendeleev, D. I., *Periodic Law*, Academy of Sciences Press, Moscow, 1958 (in Russian).
21. Mendeleev, D. I., *Principles of Chemistry*, 4th ed., part 2, St.-Petersburg, 1882 (in Russian).
22. Mendeleev, D. I., *Science archives*, vol., I, 1953, p. 654 (in Russian).
23. Mendeleev, D. I., *Principles of Chemistry*, part 2, 1871 (in Russian).
24. Mendeleev, D. I., *Principles of Chemistry*, 5th ed., part 2, 1889 (in Russian).
25. Pickering, S. U., *Ber.*, 1891, Bd. 24, S. 3629-3647.
26. Armstrong, H. E. *J. Chem. Soc.*, 1895, v. 67, p. 1122-1164.
27. Michaelis, A. *Ber.*, 1872, Jg. 5, S. 48-51.
28. Van't Hoff, J. H., *Ansichten über die organische Chemie*, Braunschweig, 1878, 214 S.
29. Lossen, W., *Ann.*, 1880, Bd. 204, S. 265-364.
30. Bezredka, A. M., *Experience of History of Development of Stereochemical Concepts*, Odessa, 1892 (in Russian).
31. Wislicenus, J., *Ber.*, 1888, Jg. 21, S. 581-585.
32. Claus, Ad., *Ber.*, 1881, Bd. 14, s. 432-435.
33. Werner, A., *Vierteljahrschr. Naturforschend. Gesel. in Zürich*, 1891, Bd. 36, S. 129-169.
34. Bykov, G. V., *History of Stereochemistry of Organic Compounds*, Nauka, Moscow, 1966 (in Russian).
35. Werner, A., *Ber.*, 1906, Bd. 39, S. 1278-1292.
36. Werner, A., *Z. anorg. Chem.*, 1893, Bd. 3, S. 267-330.
37. Werner, A., *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, Braunschweig, 1905, 189 S.
38. Werner, A., *Z. anorg. Chem.*, 1895, Bd. 9, S. 382-417.
39. Werner, A., *Ann.*, 1902, Bd. 322, H. 3, S. 261-296.
40. Grinberg, A. A., Filinov, F. M., *DAN USSR*, 1939, v. 23, issue 9, p. 918-920 (in Russian).
41. Werner, A., *Lehrbuch der Stereochemie*, Jena, 1904, 310 S.
42. Werner, A., *Z. Elektrochem.*, 1911, Bd. 17, No. 15, S. 601-609.
43. Ramsay, W., *J. Chem. Soc.*, 1908, v. 93, p. 774-788.
44. Kossel, W., *Ann. Phys.*, 1916, Bd. 49, S. 229-362.
45. *Nature of Chemical Bond and Molecular Structure*, GNTI, London, 1931, p. 4-9.
46. Kossel, W., *Valenzkräfte und Röntgenspektren*, Berlin, 1921.
47. Magnus, A., *Z. anorg. allg. Chem.*, 1922, Bd. 124, S. 289-321.
48. Fajans, K., *Z. Elektrochem.*, 1928, Bd. 34, S. 502-518.
49. Briegleb, H., *Z. phys. Chem.*, Abt. B. 1933, Bd. 23, S. 105-130.
50. Day, M. C., Selbin, J., *Theoretical Inorganic Chemistry*, 2nd ed., N.-Y., Amsterdam, London, 1969.
51. Sidgwick, N. V., *Some Physical Properties of the Covalent Link in Chemistry*, Ithaca-New-York-London, 1933.
52. Palmer, W. G., *A History of the Concept of Valency to 1930*, Cambridge, 1965.
53. Lewis, G. N., *J. Am. Chem. Soc.*, 1916, v. 38, No. 4, p. 762-785.
54. Pauling, L., *The Nature of the Chemical Bond*, 3rd ed., Ithaca-New York, 1960.
55. Ballhausen, C. J., *Introduction to Ligand Field Theory*, New York-San Francisco-Toronto, 1965.

56. Bersuker, I. B., Ablov, A. V., *Chemical Bond in Complex Compounds*, Kishinev, Shtiintsa, AN Mold. SSR, 1962, p. 208.
57. Van Vleck, J., *J. Chem. Phys.*, 1935, v. 3, p. 803-813.
58. Penney W., Van Vleck, J., Sherman, A., *The Quantum Theory of Valence*, London, 1935.
59. Basolo, F., Johnson, R. C., *Coordination Chemistry*, N.-Y.-Amsterdam, 1964. Basolo, F., Pearson, R. G., *Mechanism of Inorganic Reactions*, 2nd ed., N.-Y.-London-Sydney, 1967.

1. Formal-physical Interpretation of the Valency Concept in Pre-quantum-mechanical Electron Theories

After the electron was discovered experimentally in 1897 and proved to be a component part of the atom, the concepts of the chemical bond and valency got filled with physical sense. Kossel wrote that with the introduction of electrons, whole numbers of valency can be explained by the atomistic structure of electricity: a certain quantity of electrons take part in bonding; but the maximum valency principle shows that the number of such electrons is probably limited [1].

The elaboration of the valency concept was accompanied by consolidation of its relationship with the other concepts of the theory of atomic and molecular structure. The interpretation of chemical bond and valency becomes dependent on the model of the atom. On the other hand, the "electronization" of the classical theory of structure revealed the difficulties associated with the differences between organic and inorganic compounds. In their first scientific papers, Abegg and Bodländer [2] indicate that "the concept of atomicity of elements, and structural formulas derived with the aid of this concept and used for systematization of organic compounds, are not suitable for the same purposes in the field of inorganic compounds" [2, p. 453].

The authors suggested that the concept of electric affinity be used to systematize inorganic compounds, "because the affinity of an atom or separate groups for electric charge is more important for the existence of inorganic compounds than their affinity for each other" [2, p. 453]. As far as organic compounds are concerned, Abegg and Bodländer systematized them on the basis of the "theory of atomicity and the theory of structure".

It is also interesting to note that in this paper they indicate the existence of connection between electric affinity of an element and its position in the Periodic system. The affinity for the positive charge decreases and for the negative charge increases in the horizontal series of the natural system of elements. The series Li, Be, B, C, N, O, F begins with a strongly electropositive alkali metal and ends with a strongly electronegative halogen. Carbon, which stands in the middle of the series, has a rather indifferent character. According to Abegg and Bodländer, "the cause of its electric neutral-

ity is that it is equally indifferent towards positive and negative charges" [2, p. 453].

In his later works Abegg developed a detailed theory. First of all he introduced a new concept of electrovalency. He defined it as "valency which is determined by the number of charges carried by the ion and which is characteristic of ion-forming compounds" [3]. Then he related this concept to Mendeleev's theory of "forms of compounds of an element with hydrogen and oxygen" and the periodic law. Abegg ascribed the following numerical values of electrovalency to elements in the Mendeleev system:

Group	I	II	III	IV	V	VI	VII
Normal valency	+1	+2	+3	+4	-3	-2	-1
Contravalency	-7	-6	-5	-4	+5	+6	+7

These data were more exact numerical characteristics of elements whose absolute values were established by Mendeleev in the 1870s.

"Each element, indicates Abegg, has both positive and negative maximum valency, the sum of positive and negative units of valency always being 8; the number of positive valency units corresponds to the number of the group.... Those valency units of an element which are indicated in a smaller number (<4), and are therefore stronger, are normal valencies, whereas the units whose number is greater are weaker and of opposite polarity; these are contravalencies" [3, p. 330].

Abegg's notes concerning the relationships between the concepts of "affinity" and "valency" are also interesting. The former designates intensity, the energy of chemical aggregation, while the latter describes the number of charges which are responsible for the formation of a compound of certain composition.

The theory of Abegg-Bodländer, and similar conceptions (e.g. the one by Drude), regarded the atom as a complicate and changing object; they did not produce any model of an atom though.

But most later theories of chemical bond and valency proceeded from a more or less concrete model of the atom. The investigators usually concentrated on the mechanism of formation of the chemical bond, rather than on the valency concept. The development of theoretical chemistry during this period (from the 1890s till the middle of the 1920s) is characterized by the desire to conceive valency only through the study of the mechanism of formation of the chemical bond. Again, like in the 1860s, this led to confusion of the valency and chemical bond concepts. And it was only at the end of this period, approximately in 1923, by the time when the numerous electronic concepts were shaped into a something whole, that the problem of valency, as a relatively independent characteristic of an element or as a primary cause of chemical interaction, was again

discussed in the literature. Therefore, for a better understanding of the history of development of the valency concept during the first two decades of this century, we must dwell on some attempts to explain the nature of the chemical bond.

One of the first (after Abegg and Bodländer) models of chemical interaction belongs to the outstanding English chemist Thomson who tried to explain the formation of the chemical bond in the fact that the electrons (Thomson called them corpuscles) of electronegative atoms are held stronger than the electrons of electropositive elements.

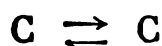
According to Thomson, the interaction between atoms results in detachment of corpuscles from electropositive atoms and their transfer to electronegative atoms. The electronegative atom will thus get a charge of negative electricity, the electropositive atoms one of positive, the oppositely charged atoms will attract each other, and a chemical compound of the electropositive and electronegative atoms will be formed [4].

The chemical bond itself is like a force tube connecting charged atoms in a molecule [5]. And valency is thus defined as the number of "force tubes" which can be formed by a given atom, and the formation of each "tube" is in turn connected with the transition of "corpuscles" (i.e. valent electrons) from one atom to another. "Corpuscles" thus correspond to valency.

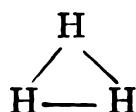
Unlike the classical valency dash, Thomson's "tube" is polar. This involved certain difficulties connected with the violation of the symmetry principle. For example, in ethane ($\text{H}_3\text{C}-\text{CH}_3$), carbon atoms are absolutely equal from the physical point of view, but according to Thomson they are different: one carries a positive and the other a negative charge. These contradictions are quite natural, because they are the result of the extension of the ionic model to those fields to which it is inapplicable.

In 1914, Thomson produced a new concept of the atomic and molecular structure, where he admitted the existence of not only ionic compounds, but also molecules where the transfer of "corpuscles" from one atom to another is absent (H_2 , O_2 , N_2 , CO_2 , CH_4 , etc.).

In such cases, according to Thomson, a dash in a chemical formula means two oppositely directed power tubes; for example, for the C—C bond of ethane he gives



This understanding of chemical bond led Thomson to the idea of possible existence of compounds "prohibited" by the classical theory of valency, e.g. the molecule H_3 :



Stark's ideas of the atomic structure and the nature of the chemical bond and valency are also of interest. Stark was more careful in proposing models than the other authors. For example, he distinguished two regions in the atom, the inner region and the surface. The problem of the structure of the inner region was, according to Stark, open to discussion, and about the same picture was with the details of the atomic surface. Here arises Stark's criticism of Thomson. The details of Thomson's structure of the atom were regarded by Stark as the disadvantage of the model and he pointed out that "an organic chemist would rather refuse any model than use Thomson's model with its inconspicuous dynamic properties for the theory of structure" [6].

Stark discussed only valent properties of atoms. He proposed a "valency hypothesis of electrical structure of the outer surfaces of chemical atoms". According to this hypothesis, "on the outer surface of a chemical atom, there are rested negative electrons, whose volumes can be assumed to be points compared with the volume of the whole atom. Such an electron emits electric power lines towards the outer surface of the atom which are directed to positive quanta in the chemical atom. If these power lines are enveloped by a surface at the closest possible distance, so that the outer electrons are outside this surface, and this surface does not cut the other parts of the atom, then electric power lines, emitted from the outer electrons, will intersect this surface at points which are larger than the section of electrons themselves. The question, what lies underneath these sites on the surface intersected by the electron power lines, remains open to discussion" [6, p. 29].

The formation of the chemical bond Stark explains as follows: "Let us imagine that two neutral atoms, each having one outer electron and spaced at a considerable distance, begin moving towards each other. The ends of the power lines of each outer electron can be directed to the positive surface of not only its own atom but of the approaching atom as well. Each outer electron, following its power lines, moves relative to the positive surfaces of its own and the other atoms, and the latter, in turn, following their own positive surfaces, move relative to each other until the outer electrons and the positive surfaces attain the equilibrium position ... at a certain distance and at a certain angle relative to each other"* [6, p. 36].

Since, according to Stark, many power lines can be emitted from each valency point, his hypothesis contradicts the classical concept of chemical force whose action is cumulated on a definite atom. In this respect Stark's views are similar to those of Thiele. Stark regards valency as an ability of an atom to form chemical bonds rather than the presence of unitary valent power (*Valenzeinzelkraft*).

* It was Stark who introduced the term "valency electrons" which is now accepted everywhere.

In 1913, Niels Bohr produced a dynamic model of a molecule [7]. According to Bohr, chemical bond arises from the presence, in free atoms, of such electrons which form a common electron orbit for two atoms; the plane of this orbit is perpendicular to the line connecting the nuclei. Bohr investigated the molecules H_2 , HCl , CH_4 , and others. According to Bohr's model the chemical bond in methane is accomplished by four two-electron orbits at the vertices of the tetrahedron. Polarity of bond (e.g. in HCl) is due to the shift of the plane of the electron ring towards one of the atoms. But despite certain vivid merits, Bohr's model was not widely recognized or developed. It was probably because the importance of Bohr's theory was not fully appreciated by chemists of that time. It was also because physicists, Bohr included, were mostly interested in the atom, and the molecular aspects were not central in the works of theoretical physicists of that time. Furthermore, Bohr's model had no connection with the theory of homopolar chemical bond. It is well known that progress in this field was made only after Bohr's hypothesis of charge distribution in the atom had been rejected.

The greatest popularity was gained by the electron theories by Kossel (Germany, 1916) [8] and Lewis (USA, 1916) [9] who, independently of each other, proposed that many atoms interact chemically because of their tendency to accept or donate electrons in the outer valence shell so that the octet of electrons, characteristic of all inert gases, beginning with neon, could be formed. However, despite the common principle of the octet, the theories are different in many respects. The differences begin with the approach to the problem. Polar compounds were Kossel's prime object since he was well aware of the difficulties associated with the description of the homopolar bond.

"We have to state, he wrote, that the only type of chemical bond whose mechanism we know and whose regularities we understand is found in heteropolar compounds. Here we have more reliable grounds than with homopolar bonds, and from this we should probably proceed in our attempts to explain the latter" [1].

When creating his system, Kossel proceeded from the following [8]:

1. Bohr's model of the atom.*
2. The electrons of the atom are divided into the outer, valency, electrons, which are responsible for the chemical interaction and optical spectra, and the inner electrons, inert in the chemical sense, which are bound with the nucleus more strongly.
3. The place of a chemical element in the Periodic system is

* At the beginning of his work [8] Kossel made some critical notes concerning Bohr's model and declared that further in his paper he would develop his own views. But the influence of Bohr's ideas can be traced throughout Kossel's system.

determined by its ordinal number which is equal to the number of units of the positive charge and the full number of the electrons in the atom. The number of electrons on the orbit increases from atom to atom in the Periodic system until the most stable configuration (e.g. the octet) is obtained, after which a new layer begins to be filled with electrons.

Kossel was, probably, the first to suggest that the elements in the atom are arranged in layers, and in his speculations he proceeded from the study of X-ray spectra (his own works included). Kossel explained the order of filling of the outer shells of the elements standing in one and the same short period, by the variations in their positive and negative maximum valency.

Kossel's ideas of formation of heteropolar bond can be summarized as follows: when two different atoms interact, they tend to stabilize their outer orbits by filling them with eight electrons. In this process one (electropositive) atom donates its electron to the other (electronegative) atom.

The valency problem was narrowed to the explanation of the ability of an atom to donate or accept electrons. Thus, the chemical approach to the study of valency should inevitably be supplemented by spectroscopical data, i.e. by the study of the arrangement of electrons, and of the regularities of formation of the atomic electron shell associated with the increasing ordinal number of the atom. The existence of certain electron groups (layers) capable of accommodating a certain number of electrons was established. This ensued from the X-ray spectra theory developed by Bohr, Moseley, Barkla, and Kossel himself.

When developing his electronic theory, Lewis approached the problem in a different way. He chose the axiomatic method, and formulated six postulates which comprised his own ideas and the ideas of his precursors:

1. Each atom contains a positively charged nucleus which remains intact in chemical reactions. The charge on the nucleus corresponds to the element position in the Periodic system.

2. The number of electrons in the outer shell of an atom varies from 1 to 8. The chemical properties of atoms depend on these outer electrons.

3. Atoms tend to form shells from even number (usually eight) of electrons, which are arranged at the vertices of the cube.

Let us consider these three postulates. Here we can see the signs of the planetary model and correct understanding of the different role of the outer and inner electrons in the chemical behaviour of the atom. On the other hand, we see an arbitrary selection of concrete arrangement of electrons. This is quite natural, because Lewis did not make use of the practical theory of Bohr, or the spectral data, and in this respect his model was a step backward.

4. Two atomic shells are mutually penetrable, i.e. an electron can enter the shell of two different atoms and can be shared by both. This postulate led Lewis to the idea that the electron shells can be stabilized to the octet not only by the electron transfer to another atom but also by sharing electrons, i.e. the atom octets can be completed without the charge transfer. This helped Lewis and Langmuir explain the formation of non-polar molecules.

5. In the cubic shell, the electron can pass from one point to another, depending on the nature of the atoms.

6. Coulomb's law does not hold for small interatomic distances, because the electron is not only an electric charge but it also has magnetic properties.

The latter idea was borrowed by Lewis from the American physicist Parsons, who postulated the complicate structure of the electron in 1915. According to Parsons, the negative charge of the electron moves by circle at a speed close to that of light, and hence should have magnetic properties.

But the cubic model could not explain the double, and especially the triple bond. This prompted Lewis the idea that in non-polar substances, whose molecules as a rule consist of atoms of small volume, the valency shells usually consist of four pairs of electrons located at the vertices of the tetrahedron, and not of eight electrons in the vertices of the cube. The tetrahedral arrangement of the atoms can be attained by placing four shared electron pairs onto four cube edges. If we now connect the cube centre with the regions of presence of electron pairs, we obtain a tetrahedron.

Lewis' ideas were developed by the American physicochemist Irving Langmuir. The theory by Langmuir is more connected with Bohr's atomic model. For example, Langmuir suggested that electrons form concentric spheric shells of equal thickness; the shells can be divided into cells, each containing not more than two electrons, and only the first shell consists of two cells with one electron in each. The electrons, according to Langmuir, are arranged as follows:

$$Z = 2 (1^2 + 2^2 + 3^2 + 3^2 + 4^2 + 4^2 + \dots)$$

i.e. a Rydberg series is formed which agrees with the length of the periods in the Periodic system of elements by Mendeleev.

The ideas of Kossel, Lewis, and Langmuir made the basis for the electron theory of valency, according to which each unit of valency corresponds to one electron in the outer shell of the atom. *The total valency of an atom in a compound corresponds to the number of electrons which form chemical bonds. The maximum valency which is possible for a given element is equal to the number of valency electrons, while the latter in turn coincides with the number of the group (of the Periodic system) where the given element belongs.*

But one must not conclude that there was full agreement among the supporters of the electronic theory of valency. In the summer of 1923 the Faraday Society organized a great discussion on the problems of the electron theory of valency. Many participants indicated that there was no unanimity among physicists and chemists in their definition of valency. Lewis, for instance, pointed out that valency can be understood as the number of bonds that a given atom can form, and as the expression of the electrical state of atoms in a given compound.

In Lewis' opinion, "If we are to regard chemistry as a single science and use the same terms in the same sense when dealing with all branches of chemistry, it seems to be only an act of justice to adopt the nomenclature so satisfactorily established by several generations of organic chemists" [10, p. 455]. "So likewise the word "valence" or "valency" should be employed, as it always has been employed by the organic chemists, to indicate the number of bonds attached to a given atom or, in accord with our newer ideas, the number of electron pairs the atom in question shares with other atoms" [*ditto*].

Opening the second part of the discussion, Robertson, the president of the Faraday Society, pointed out: "From time to time chemists used the word valency to signify the combining capacity of an atom, then they have extended it to include the strength of the union so effected, and now we are in search of a mechanism which shall explain both the numerical combining capacity and also the strength of these combining capacities by means of various rules, scarcely yet to be termed theories, for showing forth the known facts" [11, p. 484].

This ambiguity in understanding valency, and its confusion with the concepts characterizing chemical bond are another proof that the history of human thought only in general coincides with the laws of thinking, while in its particular cases it deviates from logical ways. The complicate problems of the status of the valency concept and its relation to the other concepts of the electronic theories often almost completely dissolved in the ocean of numerous concepts and models illustrating the mechanism of chemical aggregation. It should also be noted that although the theories by Kossel, Lewis, and Langmuir were fruitful from the standpoints of chemical intuition and the abundance of experimental data, they were rather primitive from the point of view of their physical substantiation. Lewis used some ideas of the planetary system of the atom and pointed out that the theory of Bohr on the whole, and of the planetary model in particular, were the most interesting and stimulating. But he was long reluctant to acknowledge the concept of stationary states, because he supposed that stability of an atom could be explained by the theory of electrostatic force equilibrium. His theory was formal, since the physical sense of the electron pairs concept

was not clear, and hence the most essential property of chemical interaction, its saturation, remained obscure. Like other pre-quantum theories, the theories by Kossel, Lewis, and Langmuir were more like the formulation of the question concerning the nature of chemical bond and valency rather than the answer to this question.

The emergence of quantum mechanics gave prospects for the solution of the valency problem by methods other than formal. But in order to give the reader a better understanding of the complicated historical way which led from the classical theory of valency, through electronic conceptions, to quantum mechanical analysis, we must return for a while into the second half of the past century and dwell on the attempts of some mathematicians to develop a formal-mathematical model which could explain all basic trends in the theory of valency and the theory of chemical structure.

2. The Emergence of the Mathematical Apparatus of the Spin-valency Theory (19th-early 20th century)

Since the time when chemistry became a science it has used mathematics as the most universal language for the expression of its laws and concepts. But along with this tendency, there exists another one: beginning with the second half of the past century some mathematicians have used chemistry to correlate mathematical structures with chemical theories, in particular with the theory of valency.

Arthur Cayley [12] was the first to work in this field. He wanted to calculate the number of possible paraffin isomers containing a given number of carbon atoms. Valency was regarded as the height of the peak of a graph (a tree) which was a mathematical expression of a chemical compound, where 1 stands for the hydrogen atom and 4 for carbon. The magnitude of valency was not at all derived from some mathematical considerations, but was postulated and introduced into the theory from chemical data. Four years later, there were published papers of the English mathematicians Sylvester [13] and Clifford [14]. They were devoted to the formal analogy which they established between the theory of chemical structure and the theory of invariants. The latter was at its start at that time. We shall not dwell on these investigations and will only consider those aspects which turned to be the "mathematical precursors" of the spin-valency theory.

Each atom X, Y, \dots was formally compared with a certain dimeric vector, e.g.

$$\begin{aligned} \text{atom } X &\sim \text{vector } \mathbf{X} = (x_+, x_-) \\ \text{atom } Y &\sim \text{vector } \mathbf{Y} = (y_+, y_-), \text{ etc.} \end{aligned}$$

A certain algebraic form can be constructed: $F = (\mathbf{X}, \mathbf{Y}, \dots)$ where the vectors $\mathbf{X}, \mathbf{Y}, \dots$ are whole non-negative exponents,

V_X, V_Y, \dots and V_I is likened to the valency of the I -th atom. This form remains invariant with respect to the unitary conversion of the components (x_+, x_-) , (y_+, y_-) , and others.*

The simplest invariant for two vectors (two atoms) X and Y is the following expression: $[x_+y_- - x_-y_+] \equiv [XY]$ which was formally compared with a single chemical bond and which first was called the monomial invariant or the bracket factor.

The monomial invariants were interpreted graphically as follows: if X and Y are designated with points on a plane then $[XY]$ is the line connecting these points.

Further, in terms of mathematics, we can introduce a certain "free" vector L . Without going into detail of the mathematical properties of L , it is possible to indicate that, graphically, the monomial invariant composed of L and of one of the "ordinary" vectors (e.g. X) corresponds to the length of a line which begins at point X and whose end remains free: $X \rightarrow L$.

The expression $[XL]$ can be interpreted as a free valency of the atom X . If the atoms X and Y are connected by a certain number (for example, K) of chemical bonds, this case can be expressed mathematically as $[XY]^K$. Likewise, a whole non-negative value f in the expression $[XL]^f$ indicates the number of free valencies of the atom X .

The product of invariants, containing no free vector, can be compared with a certain classical structural formula. But not all products of monomial invariants derived for aggregations of atoms with given valencies will be independent. A benzene molecule is a good example. Carbon atoms in benzene form a regular hexagon. Each carbon atom forms one bond with two neighbouring carbons and with the nearest hydrogen atom. According to the classical theory, carbon is tetravalent and it is therefore necessary to consider possible combinations of the residual six units of valency (one valency unit from each carbon atom).

The number of possible products of monomial invariants is considerable:

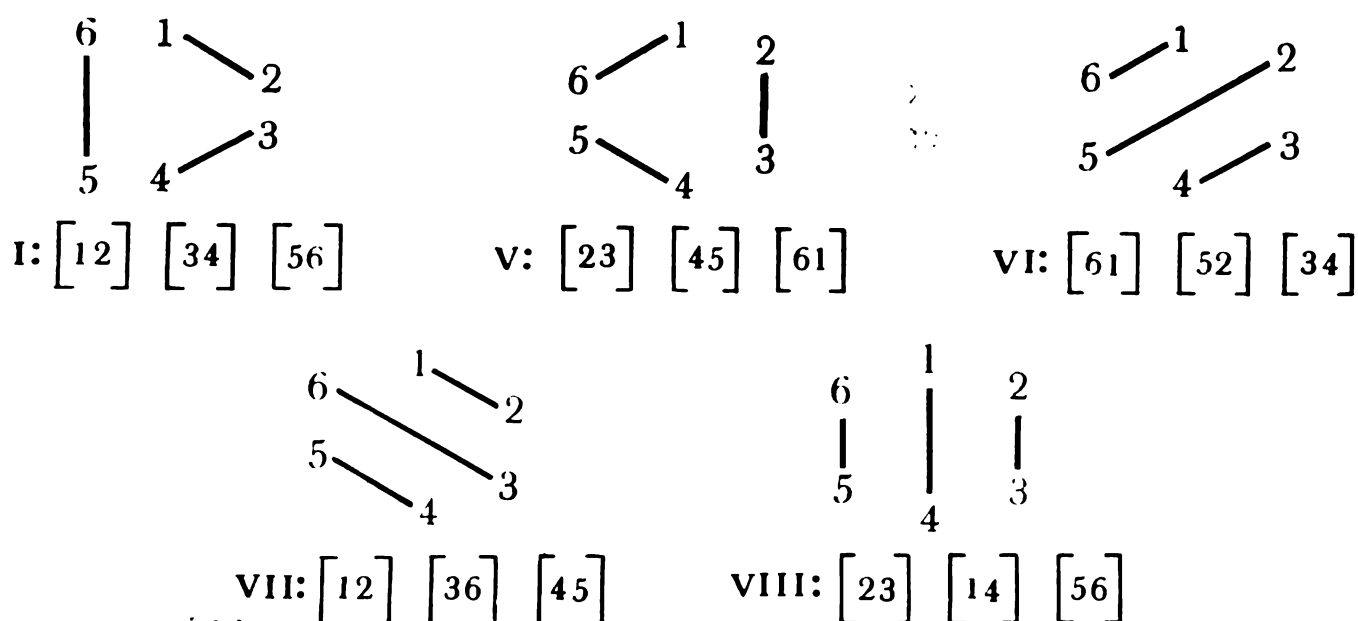
[12]	[34]	[56]	I
[12]	[35]	[46]	II
[21]	[36]	[45]	III
[13]	[24]	[56]	IV
[23]	[45]	[61]	V
[61]	[52]	[34]	VI
[12]	[36]	[45]	VII
[23]	[14]	[56]	VIII
etc.			

* Various mathematicians who developed this analogy used various forms to express it. We adhere to the form given by Weyl [15], though in some aspects we deviate from him.

But only five of them are linearly independent, e.g. I, V, VI, VII, and VIII. The other invariants can be shown in the form of a linear combination of the former five, for example:

$$\begin{aligned} \text{IV} &= [13] [24] [56] = ([12] [34] + [14] [23]) [56] = \\ &= [12] [34] [56] + [14] [23] [56] = \text{I} + \text{VIII} \end{aligned}$$

The following structures correspond to the selected linearly independent invariants:



The former two are known as Kekulé's structures and the other three as Dewar's structures.

The investigations in the "chemico-algebraic analogy" initiated by Sylvester and Clifford were then continued by the German mathematician Gordan and the Russian expert in the theory of invariants Alexeyev [16]. Although their works differ in the method of mathematical interpretation of the postulates of the theory of chemical structure, they proved to be similar in the interpretation of the valency concept, which can be characterized as follows:

(a) valency of a given element is derived from chemical, not from mathematical considerations;

(b) valency is considered as the sum of multiple bonds formed by a given atom with other atoms, the unit of chemical bond between the atoms X and Y being regarded as a monomial invariant $[XY]$.

This analogy was sceptically met by some mathematicians (Netter, Study [17]). Study, for example, wrote that "it would be fantastic to expect that chemistry might take any advantage from this branch of algebra" [18]. But the situation changed with the emergence of quantum mechanics. In the 19th, and early in the 20th century, it was nothing but a formal, though a conspicuous and impressing

mathematical analogy (Weyl). But late in the 1920s this is already an essential line in the quantum mechanical theory of chemical bond, in which this analogy has a surprizingly concrete embodiment (Weyl).

3. The Valency Concept in the Valence Bond Method

After Heitler and London explained in 1927 [19] the nature of chemical bond in a molecule of hydrogen from the standpoints of quantum mechanics, some investigators [20] made attempts to extend their ideas to more complex systems, and this gave the method of valence bonds (VBM). Although the method is not optimum for quantitative calculations, it nevertheless produced a marked effect on the development of the quantum theory of valency, which made it very popular among chemists, especially among organic chemists.

The main idea of the VBM consists in the assumption that atoms, or, to be more exact, atomic orbitals, preserve their specific features in a molecule. The orbitals of separate atoms A, B, . . . , which are at a finite distance from one another, but which are conventionally assumed to be non-interacting, compose the many-electron spin-free function, the product

$$\Phi = \varphi_{a_1}(\vec{r}_1) \dots \varphi_{a_p}(\vec{r}_p) \varphi_{b_1}(\vec{r}_{p+1}) \dots \varphi_{b_q}(\vec{r}_{p+q}) \dots$$

$$\begin{array}{c} a_i \in A \\ b_i \in B \\ \dots \end{array}$$

Generally speaking, $\varphi_{a_1}, \dots, \varphi_{a_p}$ can be not the orbitals of a free atom A, but their linear combinations, i.e. hybrid atomic orbitals.

The combination of all orbitals φ is called the configuration, and each sub-combination $\varphi_{a_1}, \dots, \varphi_{a_p}$ is the valent configuration Γ_A of the atom A. Some atomic orbitals φ enter into Γ_A twice and are called paired. The number of unpaired orbitals in the configuration Γ_A is known as spin-valency of the atom A in the corresponding valency state. Function Φ is multiplied by the function $\Theta(\sigma_1, \dots, \sigma_N)$ which depends on spin variables of all electrons.

To each atomic orbital (AO) φ there correspond two single-electron spin functions $\alpha(\sigma)$ and $\beta(\sigma)$ which are the eigenfunctions of a single-electron projection operator of the spin momentum onto the axis of quantization \vec{n} :

$$\left. \begin{array}{l} \hat{S}_n \alpha(\sigma) = +\frac{1}{2} \alpha(\sigma) \\ \hat{S}_n \beta(\sigma) = -\frac{1}{2} \beta(\sigma) \end{array} \right\}$$

The many-electron function Ψ which determines the electronic state of a molecule must be an eigenfunction for the square operator of the full spin momentum \hat{S}^2 of the N -electron system of the molecule. Since the operator \hat{S}^2 acts only on the function $\Theta(\sigma_1, \dots, \sigma_N)$ the above condition imposes certain limitations only onto Θ , and not onto $\Phi(\vec{r}_1, \dots, \vec{r}_N)$ (\vec{r}_i is the spatial coordinate of the i th electron).

Most stable substances consist of molecules with zero full spin, i.e. occur in the singlet state. For the sake of simplicity we shall further discuss only such molecules.

The function Θ is constructed from single-electron spin functions as follows:

(a) a pair of functions $\alpha(\sigma)$ and $\beta(\sigma)$ compose the two-electron function

$$\gamma(\sigma_i, \sigma_j) = [\alpha(\sigma_i)\beta(\sigma_j) - \beta(\sigma_i)\alpha(\sigma_j)]/\sqrt{2}$$

where σ_i and σ_j are spin variables of the i th and j th electrons;

(b) by multiplying $N/2$ functions γ , which depend on spin variables of various electrons, we obtain the function $\Theta_\kappa(\sigma_1, \dots, \sigma_N) = \gamma(\sigma_1, \sigma_2) \dots \gamma(\sigma_{N-1}, \sigma_N)$.

The necessity of indexation of the function Θ arises from the multitude of its possible variants constructed from the function γ . For the system of N electrons, it is possible to construct $n!/[(n/2)!(n/2 + 1)!]$ linearly independent Θ_κ , where n is the number of unpaired AO in the system.

For example, for the π -electron system of benzene, comprising six electrons (and the same number of atomic π -orbitals) it is possible to construct $6!/[(3!4!)] = 5$ independent functions Θ_κ .

Thus we have to consider the function of the type

$$\Psi = \Phi(\vec{r}_1, \dots, \vec{r}_N) \sum_{\kappa} \Theta_{\kappa}(\sigma_1, \dots, \sigma_N) C_{\kappa} \quad (A)$$

comprising numerical factors C_{κ} , which are determined by the minimization of full electron energy of the molecule.

Of course, the function of the state of the N -electron system must be antisymmetrical with respect to possible rearrangements of the electron coordinates*. The function (A) does not meet this condition and should therefore be antisymmetrized.

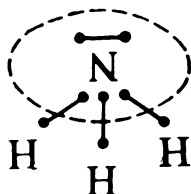
Since the function Φ is the product of orbitals $\varphi_i(\vec{r}_i)$, this procedure preserves the correspondence between the pair of orbitals (φ_i, φ_j) and a certain spin function γ for each component in the sum (A), which is characterized by a certain index κ and known as

* Here we mean re-arrangement of N sets $(x_i y_i z_i \sigma_i)$ each of which comprises three spatial $(x_i y_i z_i)$ and one spin (σ_i) coordinates of the i th electron.

structure. We can therefore state that orbitals φ_i and φ_j in a certain structure κ are paired.

If each orbital φ_i is compared with a point on a plane, then the process of pairing of two orbitals can be shown by a length of line connecting two corresponding points.

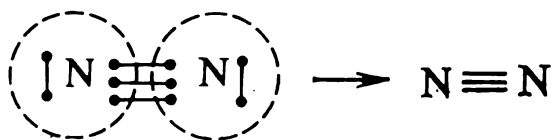
For example, one of the structures of the ammonia molecule NH_3 can be shown by the following diagram of the orbital bonds:



The dotted line here encircles a group of points which correspond to the orbitals of the nitrogen atom. If we pull this group into one point we obtain the following diagram of atom bonds:



Likewise, for a molecule of nitrogen N_2 , we have



In some cases the electronic structure of a molecule can, to a sufficient degree of accuracy, be described by one structure. Then multiplicity of atom bonds is identified with the number of dashes which connect the points corresponding to the atoms on the bond diagram, and the diagrams themselves (of the B type) become identical to chemical structural formulas.

In other cases it is necessary to account for several structures. For example, in a molecule of benzene, it is necessary to consider at least two Kekulé's structures. In such "non-classical" cases, bond multiplicity is averaged for structures in accordance with the weight w_κ of each structure κ in the resolution of the many-electron function Ψ :

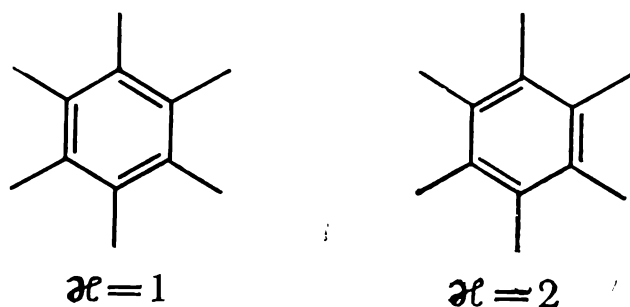
$$K_{AB} = \sum_{\kappa} w_{\kappa} \sum_{a \in A} \sum_{b \in B} k_{ab}^{\kappa}$$

where $k_{ab}^{(\kappa)} = \begin{cases} 1, & \text{if atomic orbitals } a \text{ and } b \text{ are paired in the structure } \kappa; \\ 0 & \text{in the opposite case;} \end{cases}$

w_κ is the weight of the structure κ ;

A and B are atoms and the corresponding sets of atomic orbitals.

Weights of structures depend, generally speaking, on both the coefficients C_κ and on the overlap of the corresponding many-electron functions. The latter are not orthogonal and the concept of the weight is therefore not a simple one. Unfortunately there is no satisfactory definition of this concept. But in some cases, weights of structures are determined from their symmetry exclusively. For example, for the π -electron system of benzene, the weights w_κ of two Kekulé's structures are equal because these structures are equivalent with respect to symmetry. Therefore, if we disregard other structures, then $w_\kappa = 0.5$ ($\kappa = 1$ and 2):]



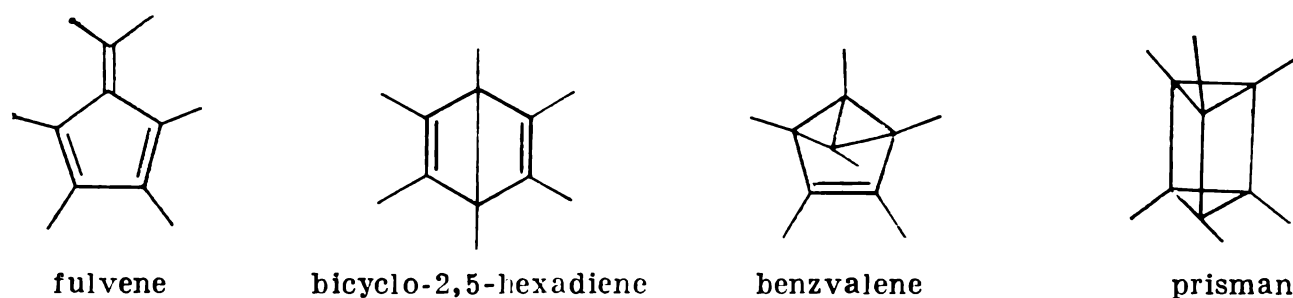
and if we consider the σ -system, which is described by only one structure, the multiplicity of the bond of two neighbouring carbon atoms is

$$K_{C_i C_{i+1}} = 2 \times w_1 + 1 \times w_2 = 1.5$$

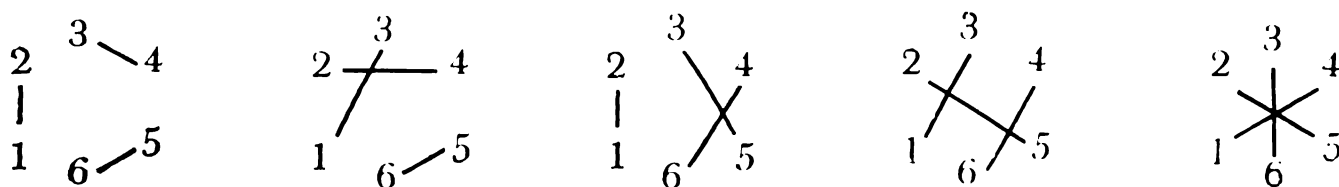
Similarly for two neighbouring atoms of carbon and hydrogen:

$$K_{C_i H_i} = 1 \times w_1 + 1 \times w_2 = 1$$

Unlike benzene, for whose π -electron system it is necessary to account for at least two structures, its valent isomers can be characterized by one diagram (or structural formula), for example:



A problem, which is more difficult than the determination of weights of non-equivalent structures, is the selection of structures themselves. For the π -electron system of benzene, the linearly independent basis can comprise five structures characterized by the following diagrams:



These diagrams correspond to Young's tableaux:

1	2	1	3	1	2	1	3	1	4
3	4	2	4	3	5	2	5	2	5
5	6	5	6	4	6	4	6	3	6

Each tableau has two columns of numbers of atomic orbitals (in their increasing order). The second number in any row must be greater than the first one. The number of standard tableaux is equal to the number of linearly independent many-electron spin functions obtained by pairing single-electron functions.

Young's tableaux are very convenient for isolation of a linearly independent set of structures, especially when the task is not limited to consideration of the π -electron sub-system and the number of electrons is great.

Evidently, whatever the weights of these structures may be, π -electron constituents of multiplicity of bonds C_2C_3 , C_4C_5 , and C_1C_6 are zero, and hence these bonds, unlike the bonds C_1C_2 , C_3C_4 , and C_5C_6 , are the ordinary ones. Multiplicities of the other bonds do not agree with the symmetry of the benzene molecule either. Kekulé and Dewar's set of structures for benzene can give us reasonable values for bond multiplicity. But in the general case the formulated problem is not yet solved.

The valency of the atom A can be determined as a sum of multiplicities of bonds formed by the atom A:

$$V_A = \sum_{B(\neq A)} K_{AB} = \sum_{B(\neq A)} \sum_{\kappa} w_{\kappa} \sum_{a \in A} \sum_{b \in B} k_{ab}^{(\kappa)} = \sum_{a \in A} \sum_{\kappa} w_{\kappa} V_a^{(\kappa)}$$

Here

$$V_a^{(\kappa)} = \sum_{B(\neq A)} \sum_{b \in B} k_{ab}^{(\kappa)} = \begin{cases} 0 \\ \text{or} \\ 1 \end{cases}$$

is the contribution of the atomic orbital $a \in A$ to the valency of the atom A which can be called partial valency of this orbital.

In the VBM, with the only valent configuration Γ_A for each atom A (without accounting for the ionic structures) the magnitude $V_a^{(\kappa)}$ does not actually depend on κ for singlet states. In view of this circumstance and also of the fact that the weights of all structures are equal to unity, the valency of the atom can be expressed as the sum of partial valencies of its orbitals:

$$V_A = \sum_{a \in A} \left(\sum_{\kappa} w_{\kappa} \right) V_a = \sum_{a \in A} V_a$$

In accordance with the latter equation, the valency of the atom A is equal to the number of unpaired orbitals in the valency configuration Γ_A of this atom (spin-valency) and does not depend on the chosen set of structures or the method by which the weight of separate structures is determined.

To return to the formal "chemico-algebraic" analogy we can state that its physical sense was disclosed in the method of valent bonds. It turned out that the bicomponent vector $X = (x_+, x_-)$ corresponds to a pair of single-electron spin functions $\alpha(\sigma)$ and $\beta(\sigma)$; the monomial invariant $[x_+y_- - x_-y_+]$ corresponds to the dielectron spin function $[\alpha(\sigma_i)\beta(\sigma_j) - \alpha(\sigma_j)\beta(\sigma_i)]$ which, at the time of the emergence of quantum chemistry, was known as the spin-invariant; the product of the monomial invariants raised to the appropriate powers corresponds to the concept of the structure in the VBM; and finally, valency, as the exponent of V_X , in which X enters into $F(X, Y, \dots)$, corresponds to the number of unpaired orbitals in the valency configuration Γ_X .

Thus, the formal model of the valency theory, developed by several mathematicians during 1878-1902, was a preliminary stage in the development of the mathematical formalism of the VBM. Although not substantiated physically, based only on the values of valencies borrowed from chemistry, this model correctly reflected the general character of those mathematical structures which were later used in the quantum chemical method of valence bonds for the description of chemical structures.

References

1. Kossel, W., *Über die Physikalische Natur der Valenzkräfte*, Naturwissenschaften, 1919, 7, Jahrg., S. 339-345; 360-366.
2. Abegg, R., Bodlander, G., *Z. anorg. Chem.*, 1899, Bd. 20, S. 453-499.
3. Abegg, R., *Z. anorg. Chem.*, 1904, Bd. 39, S. 330-380.
4. Thomson, J. J., *Phil. Mag.*, 1904, ser. 6, v. 7, p. 262-263.
5. Thomson, J. J., *Electricity and Matter*, Edinburg-N.Y., 1904, p. 83.
6. Stark, J., *Prinzipien der Atomdynamik*, III Teil: Die Elektrizität im chemischen Atom, Leipzig, 1915, S. 58.
7. Bohr, N., *Phil. Mag.*, 1913, v. 26, p. 1-25, 476-502, 857-875.
8. Kossel, W., *Ann. Phys.*, 1916, Bd. 49, S. 229-241.
9. Lewis, G. N., *J. Amer. Chem. Soc.*, 1916, v. 38, p. 762-785.
10. Lewis, G. N., *Trans. Farad. Soc.*, 1923, v. 19, p. 455-485.
11. Robertson, R., *Trans. Farad. Soc.*, 1923, v. 19, p. 484-485.
12. Cayley, A., *Phil. Mag.*, 1874, v. 67, p. 444-447.
13. Sylvester, J., *Amer. J. Math.*, 1878, v. 1, p. 64-104.
14. Clifford, W., *Amer. J. Math.*, 1878, v. 1, p. 126-127.
15. Weyl, H., *Philosophy of Mathematics and Natural Sciences*, Appendix D., Princeton Univ. Press, 1949, 220 p.

16. Gordan, P., Alexejeff, W. *Z. phys. Chem.*, 1900, Bd. 35, S. 610-633.
17. Study, E., *Z. phys. Chem.*, 1901, Bd. 37, S. 546-647; Alexejeff, W., *Z. phys. Chem.*, 1901, Bd. 38, S. 750-752.
18. *Encyklopädie der mathematischen Wissenschaften mit Einschluss ihrer Anwendungen*, Bd. 5, Physik, T. I.; C., Molekularphysik III, Anhang, S. 385-388.
19. Heitler, W., London, F., *Z. Phys.*, 1927, Bd. 44, S. 455-472.
20. Heitler, W., Rumer, G., *Nachr. Gött. Math.-Physik.*, 1930, H. 3, S. 277-284; Rumer, G., Teller, E., Weyl, H., *Nachr. Gött. Math.-Physik*, 1932, H. 5, S. 499-504.

Chapter Six Manifestation Forms of Atom Valency Potentialities

1. Valency as Empirical Invariant of Atom Properties

One of the possible approaches to the valency problem is the discussion of valency as one of the main properties of the atom. As a rule, by the main property of an atom or an element [1] is understood the qualitative and quantitative property which remains relatively unaltered as the atoms of a given element pass from one compound into another.

Mendeleev held that the main quantitative property of an atom is its atomic weight (atomic mass). In the history of chemistry, the atomic mass remained for a long period of time (since the development of Dalton's theory) the only property of an atom which does not depend on the surroundings. Of course, Dalton himself (in his earlier works) and his precursors, the atomists of the 17-18th centuries (in their dynamic systems), ascribed some other properties to the atom, such as dimension, shape, thickness of the thermogenic layer, etc., but all these properties were quite arbitrary and hypothetical in character, and could not be proved quantitatively by experience with a sufficient degree of certainty.

The dynamic corpuscular atomistics (the philosophy of peaks and hooks) did not lead to constructive systems of chemical knowledge. But Dalton's physico-theoretical understanding of the atom and element [2], which was based on quantitative experimental data, was more important for the development of chemistry. However, as the time went on, Dalton's theory could no longer satisfy the chemists either because it was insufficient to have only one quantitatively measurable property, *viz.*, the mass, in the general system of qualitative concepts of the dependence of substance properties on its composition and structure. This is why, beginning with the nineteenth century, chemists, in their attempt to find some other properties of the atom which could be interpreted quantitatively, undertook an intense research in the physico-chemical properties (known at that time) of as many compounds as possible. This can be called the attempt to find quantitative invariants characterizing the atom of a given element in large groups of compounds (if not in all compounds).

The most intense search for such invariants was undertaken early in the nineteenth century. It was directed mainly at densities (volumetric properties of bodies) and heat capacities. Many investiga-

tions were carried out in the field of boiling and melting points of substances, and later in the field of refractive index, heat of formation, magnetic and electrical properties, etc. The history of development of this trend of physical chemistry is of independent interest, and here we should only like to note that all these investigations were aimed at finding of a quantitative effective contribution (increments) of the atom of a given element to the overall property of a complicate compound. In the simplest case this might be the property of a simple body (elementary example of additivity), and in other cases, it might be a certain value which could be calculated by comparing the properties of some similar substances and remains unchanged in the series of such compounds (increment of properties). It was this trend in the investigations of quantitative properties that led to the discovery of the main physico-chemical regularities and to the formation of the modern system of knowledge which make up the subject matter of physical chemistry and which is based on thermodynamics, statistical physics, and quantum mechanics.

The results of the search for atomic invariants of physical properties were rather modest. But the investigators found a certain number of additive and correlative functions which made it possible to predict the properties of a compound from the properties of its component elements or fragments (refraction, parachor, critical parameters, diamagnetic susceptibility, etc.). But these characteristics were of relative value as criteria of basic properties or quantitative invariants characterizing atoms or groups, because it was very difficult to differentiate between the properties related to atoms and those which depended on their surroundings.

The new approach to the problem of the main property which would give a new look at the atom in a compound became possible only in the middle of the nineteenth century with the transition of chemistry to a new conceptual system [3]. In fact, all above mentioned investigations did not extend beyond the limits of the first (historically) method by which the problem of etiology of properties of chemical individuals was solved (i.e. beyond the limits of the composition-property relationships). Of course, this method is still important in our days. But it does not include the structural parameter which can characterize the atom from quite different positions. The new approach could therefore be realized only with the "second conceptual system" comprising the structural factor. Here the main emphasis is laid on the ability of atoms of a given element to combine with a certain number of other atoms or atom groups, i.e. the valency (atomicity) of elements emerges here.

It is easy to notice that valency refers to the atom and can therefore be regarded as one of its basic properties. And Mendeleev used therefore this modified concept of valency ("form of compound") as the main function to formulate his periodic law. On the other

hand, a vividly quantitative character of valency was always regarded also as an invariant characterizing the atom of a given element. In contrast to the invariant of quantitative physico-chemical properties it could, more exactly, be named the topological invariant.

Valency, at least at its first, purely empirical level, has much in common with various quantitative increments of properties which we mentioned above. In fact, a system of three atoms AB_2 can be shown by various systems of valency distribution by chemical bonds (structure graphs): linear form $A''(B')_2$ and triangular $A''(B'')_2$. The number of variants increases even more if the concept of bond multiplicity is involved.

So, concrete determination of valency of a given atom was based on the corresponding propositions of structural theories explaining the bond distribution systems: the valency of one, two or three elements must be constant and known. This assumption (although not always spoken out openly), admitting the existence of a certain number of "choice" elements, which preserve their valencies unchanged during formation of compounds, explains the close relationships between the concepts of valency and increments of physico-chemical properties. So, the fact that a given element may have variable valency is not the most important one: valency varies only within a certain range and this range itself can be regarded as invariant. The main point is that when an element occurs in a series of similar compounds, it must retain constant valency. For example, in a series of oxides the "choice" element is oxygen. But for many complicate structures it is necessary to determine beforehand "standard" valencies of other elements (sulphur, phosphorus, etc.). For example, valencies of elements forming sulphates and sulphites are determined by oxygen which is assumed to be divalent; this assumption is however insufficient to determine the formal valency of sulphur which forms thiosulphates and polythionates.

Thus, the arrangement of similar compounds in a series depends on the validity of the assumption of constancy of valency of a given element in the compounds of this series.

It is not therefore surprising that the discovery of new classes of compounds widens the concept of valency, its definitions extend and grow in number.

To summarize, we shall name the factors by which two different characteristics, namely, the ability of a free atom to form compounds, and the status of the same atom in a compound, were united into the concept of valency. These factors are:

(a) the desire to see in valency another characteristic of invariant "basic" properties of elements, as is the atomic mass;*

* To be more exact, the atomic mass is not an invariant either because the masses of atoms in the free and bound states are not the same (the mass defect is about 10^{-10} atomic mass units).

(b) the emergence of the valency concept was stimulated by the demands of the developing structural theories and the new concept was immediately used by theories describing chemical bond;

(c) valency numbers, i.e. the number of affinity units of a free atom on the one hand, and the number of bonds formed by the same atom in the bound state on the other hand, coincide in most cases, especially in organogenic elements (C, H, O);

(d) unlike the atomic mass, valency played an important role as a characteristic of properties which are invariant only when applied to certain series of chemical individuals, these series comprising also "simple bodies".

It is also evident that classical chemistry, and its structural theories in particular, needed valency first of all as a basis to form the concept of chemical bond and of the order of chemical bond rather than to characterize chemical bond itself. It is necessary to emphasize that the search of invariant properties of elements, and the inclusion of valency into such properties, arose from the theory of chemical elements, i.e. from the theory of composition of chemical compounds rather than from structural theories. The theory of chemical structure, with its main thesis of the mutual effects of atoms in a molecule, had a different object: the study of changes in reactivity of atoms in a compound where they mutually transform one another. In spite of this circumstance the structural theories became a stimulus for the development of the valency concept. The theory of structure needed valency as a spring-board.

2. Electronic Interpretations of the Valency Concept

What we have said about the formal character of valency does not deprive this concept of its real physical sense. The development of many substantiated general concepts often passes the stage of effective empirical increments which are then given certain physical substantiation. It should be understood that such substantiation cannot occur at once but only in steps. In some cases complete and comprehensive explanation of a phenomenon is possible, whereas in other cases the theory must limit itself to qualitative descriptions only. As a result, even the modern concept of valency, in both theoretical and empirical aspect, remains a many-sided and not fully coordinated concept. Being applied to various chemical systems, and based on the results of investigations of substances by different methods, the concept of valency becomes a complicate logical structure, the complexity of which becomes apparent at the first acquaintance with chemistry.

The theoretical concept of valency is not a simple substantiation of an empirically discovered phenomenon, but can be regarded as a certain independent conception which is a logical effect of the theory of structure of the electron shell of the atom. This conception, at least in general, can describe deductively valency potentialities of a given atom. Nevertheless, in reality this situation can be considered as ideal which we must try to attain. Valency "potentialities" of atoms are so immense that probably not a single theoretician, assisted as he is with the modern quantum-mechanical calculation technique, will ever dare predict stoichiometry of any more or less complicate stable structure. Of course, it is easy to explain this stoichiometry once it is known from experiment [4].

Indeed, the attentive consideration of the problem shows that, from the structure of an individual free atom (i.e. in its ground, unexcited state, when the atom is not acted upon by any force) one can suppose the possible formation of compounds of various composition and explain manifestation of practically unlimited valency potentialities in any atom. The main idea which should only be borrowed from experience is the idea of saturation. Indeed, the fundamental principle of limit, which is so important in chemistry, is difficult to interpret from purely theoretical standpoints, and a theory will easier and more logically explain the expansion of the valency potentialities of an atom rather than their narrowing.

At the present stage of science, after the emergence of chemistry of "noble gases", the inertness of the noble gases, from theoretical point of view, seems to be much more surprizing than their ability to give complicate structures.

In view of all what has been said, there arises the possibility of a new approach to the valency concept from the *apriori* suggestion of polysemantic complexity of the concept. We can consider the conditions under which various valency potentialities of an atom can be realized. These are latent in some cases and quite vivid in other. In other words, it is interesting to establish a kind of hierarchy of valent structures. Probably, this hierarchy will in a certain form reflect the evolutionary development of the chemical form of organization of matter [3]. It is quite possible that in nature itself, in the process of gradual complication of chemical systems, certain conditions could have been created, under which the latent abilities of atoms or groups of atoms to form new valent structures were realized. Such a picture of consecutive growth of the variety and complexity of manifestation of valency make unnecessary any universal definition of valency. Such a definition can hardly be constructive at the present time.

It is useful to correlate the general picture of such "development" of valency potentialities with the position of elements in the Periodic system. It is expedient to remember the work by Yatsimirsky [5]

where he considers the consecutive involvement of various types of bonds in complex compounds in the downward direction in the groups of the Mendeleev Periodic system. Thus, according to Yatsimirsky, only σ - and π -bonds can be formed in complexes of the elements of periods I-III. π -Acceptors and the metal-metal bonds appear in the elements of the fourth period. And finally, the formation of stable clusters becomes possible in the last periods.

An interesting example illustrating the changing ability of elements to form bonds (i.e. complication of types of valency interactions) is a series of the elements of the main sub-groups arranged in the order of their increasing atomic masses. Let us remember the structure of simple "bodies" in the 5th or 6th group

N	O
P	S
As	Se
Sb	Te
Bi	Po

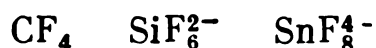
The first members of the groups form diatomic molecules with multiple bonds, but stable bonds are less characteristic of next elements (molecules P_2 and S_2 are unstable). Single bonds in tetrahedrals (P_4 white) or in cycles (S_8) are more characteristic. And finally, signs of bond delocalization appear. The characteristic feature of changes in the type of interaction inside the group is certain "diffusion" of bonds, i.e. the increasing number of directly connected atoms. As the atomic number increases, the valency forces tend to distribute by the increasing number of bonds. For example, for nitrogen and oxygen, all energy of interaction is concentrated along the line of one two-centre bond (N_2 , O_2); and further go three (P_4) and two (S_8) ordinary bonds. Finally, at the end of the groups, the coordination numbers exceed valency, and it becomes possible to consider (at least formally) multiplicities less than unity (fraction of the "bonding force unit"), which is equal to the formal valency divided by the coordination number, according to Pauling.

Said tendencies are an example of concrete analysis of the changes in the methods of bonding or types of realization of valencies which occur in the transition from one element to another. The transitions are varied in character and their more or less comprehensive description cannot be the subject of this work. In this book we shall only dwell on some aspects connected with the peculiar "splitting" of the valency concept, which (although it seems to be an integral concept) appears to be a polysemantic phenomenon requiring much additional information to form a single-meaning concept. Such a situation occurs probably in cases where the concept of valency, developed on the basis of one category of elements, is transferred onto another

category characterized by a different structure of electron shells. For example, it is trivial now to discuss the principal difference between the fifth oxidation degrees of nitrogen and phosphorus in such forms as E_2O_5 or X_3EO (where E is N or P). It is necessary to remember that in the case of nitrogen, one of the oxygen atoms is connected by a single bond. At the same time, the corresponding interaction of phosphorus with oxygen is characterized by multiple bond. Thus, although in both cases we have formally identical fragments $E=O$, the nature of the interaction of nitrogen and its analogue phosphorus differs substantially.

At the present time very popular is the opinion that *d*- and *f*-orbitals take part in the formation of bonds in the downward direction in the groups of the Periodic system.

It is very easy to explain many phenomena using this model, for didactic purposes in particular [6]. In fact, no matter what particular model is assumed, we can state that the character of interaction between the elements in identical forms, EO_m , EX_n , etc., changes substantially in the downward direction in the groups of the Periodic system. This produces a marked effect on stability of the corresponding compound forms (the rules by which stability of compounds of elements of higher valency decreases in the main sub-groups, and increases in additional sub-groups of the system; also the rule of the secondary periodicity) and particularly on the growth of the coordination number in complex compounds. Consider the following binary compounds of the fourth group elements:



The oxidation degree of the central atoms is the same in all these compounds (4), but the nature of the interaction between the central atom and the ligand differs substantially. After all we can state that the "valency states" in C(IV), Si(IV) and Sn(IV) are different, meaning that there exist more or less significant differences in the character and number of atomic orbitals which take part in the interaction (or the different extent of utilization of *d*-, *f*-orbitals). It should be noted, however, that the term "valency state" is commonly used in a slightly different sense in quantum mechanics. Therefore, drawing a distinct boundary line between the concepts of "valency" and "valency state" will not ensure the required accuracy of differentiation, especially so that "oxidation degree" and "atomicity" are quite real concepts.

Without going into detail of this interesting problem, we shall proceed to another characteristic example of "splitting" of the valency concept in the transition to the atom with a new structural type. Consider a solid oxide EO_2 . If E is an element belonging to the main sub-group of the fourth group, e.g. silicon, we can say that tetravalent state is realized here. But as we pass over to the

elements of the additional sub-groups having higher valencies, e.g. chromium, the problem becomes markedly more difficult. It is reasonable to admit the existence of a certain averaged valency for chromium in CrO_2 , where only formally it can be assumed to be four. It does not correspond to the "true valency" of separate chromium atoms in this compound. Aria [7], in this connection, thinks it necessary to strictly differentiate between "true valency", which is the "number of orbitals used by the given atom to form bonds" from "formal valency" corresponding to stoichiometry of a compound. In our case the "true valency" of chromium is probably three and six simultaneously. And it is easy to understand that such an alternative is absent in the case with SiO_2 .

It is especially important to distinguish between "true" valency of atoms and "formal" valency, calculated from the formula of a compound in cases where the proportion of one of the valency states is small. For example, the presence of two states, Fe^{2+} and Fe^{3+} , in iron monoxide phase ensures a homogeneous region (the compound $\text{FeO}_{1\pm x}$), i.e. a compound of variable composition. Here the "formal" valency (if we only can insist upon this term) has no sense, while "true" valency requires special experimental and theoretical methods to be determined.

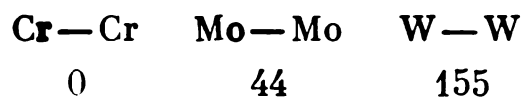
We can conclude in general that the incidence of complicate atomic interactions increases in the downward direction in the groups of the Periodic system, the classical methods of determining valency being of little use in such cases.

Consider the formation of clusters, which are relatively independent structural groupings of atoms in solid complex chlorides of many transition metals. The complex $[\text{Nb}_3\text{Cl}_{13}]^{5-}$ is an example of such clusters. The classical method of calculating formal valency of niobium in this complex gives the fractional answer: $(13 - 5) : 3 = 2.66$. At the same time, this calculation does not account for a significant characteristic of cluster structures: formation of the metal-metal bonds.

A detailed structural analysis and quantum mechanical calculations show that here the central atoms utilize all their valency electrons. They are five in our example. Thus niobium remains pentavalent in this complex. Of the total number of valency electrons ($3 \times 5 + 13 + 5 = 33$) 26 are used to form the Nb—Cl bonds and 7 to interconnect the niobium atoms between themselves (metal-metal bonds). Each of the three Nb—Nb bonds is thus formed by 2.33 electrons.

It is evident that the classical concept of valency and the formal approach do not hold here. Here we face the delocalization of electrons by several bonds. It is also evident that this property of atoms increases substantially in the downward direction in the groups of the Periodic system. Stability of cluster structures increases as well.

According to Korolkov [8], the energy of the metal-metal bond (kilocal) increases significantly in clusters of the sixth additional sub-group:



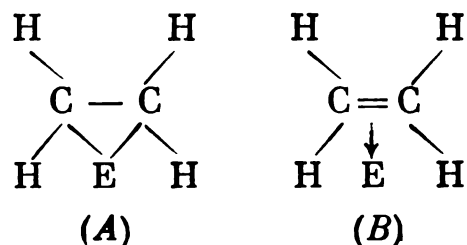
The increasing ability to form clusters expresses the general tendency of strengthening metal properties in the downward direction in the groups of the Periodic system. In cases where the metal bond can be realized, it strengthens in the downward direction in a given group. For example, the energy of the metal-metal bond in dinuclear carbonyls of the $\text{E}_2(\text{CO})_{10}$ type increases as follows [9]:



It is clear that the metal bond arising from a considerable delocalization of electrons reflects the general tendency of complication of forms of valency interaction and deviation from the classical concepts of valency.

The delocalized bond between the atoms of the transition metals and organic molecules with unsaturated bonds is probably another manifestation of the same tendency. This type of organo-element compounds is being thoroughly studied at the present time and is another vivid example how the transition to new types of structure changes the existing concept of valency interactions.

Consider a compound of a simple unsaturated ethylene molecule with platinum as an example. It is interesting to note that the attempt to determine valency of the platinum atom (from the aspect of the electronic concept) in this compound gives an alternative conclusion. Indeed, it is possible to regard the system platinum-ethylene either as a particle with two σ -bonds (A) or as a system with the overlapping of electron clouds of d -orbitals of platinum with π -orbitals of ethylene (B). In the former case platinum is sometimes regarded as a divalent metal and in the latter as zero-valent [10]:



Delocalization of the bond is evident, and the opinion that the platinum atom interacts with separate atoms of ligands, like hydrogen interacts with carbon in methane, is insolvent.

It is necessary to point out that the tendency of the transition metals to form compounds with unsaturated molecules increases in the downward direction in the groups. This is proved indirectly by some experimental data and especially by thermodynamic characteristics of bonds. The dissociation energy of the E—CO bond in mononuclear carbonyls, which are compounds with unsaturated molecules as well, markedly increases in the group in the downward direction:

Cr(CO) ₆	29.5 kcal
Mo(CO) ₆	35.9 kcal
W(CO) ₆	42.0 kcal

Bis-arene compounds probably give the same picture [9]:

(C ₆ H ₆) ₂ Cr	40.0 kcal
(C ₆ H ₆) ₂ Mo	51.0 kcal

So the downward variation in the groups is, as one might expect, characterized by the complication of valency interactions, by greater deviation from the classical two-centre bonds, and by inapplicability of formal concepts.

3. Dependence of Forms of Valency Potentialities on the Electron Structure of Free Atoms

The mentioned tendency must undoubtedly depend on some deep changes in the atom structure. An important manifestation of these changes is the increasing role of *d*- and *f*-orbitals and their mixing with the outer *p*- and *s*-orbitals. For example, participation of *d*-orbitals in the outer electron layers is characteristic of lanthanum at the beginning of the series of the rare earths, but in the next family, the actinides, it is characteristic of almost half of the elements at the beginning of the series (Ac, Th, Pa, U, Np).

Theoretical calculations show that in super-heavy elements, beginning with the eighth period, this mixing of orbitals, characterized by various quantum numbers of the orbital momentum (*l*), becomes even more pronounced. It is shown [11] that 8*p*-orbitals are split in the eighth period and part of them is filled. The elements which, in accordance with the general law of periodicity, had to start filling *g*-orbital, start, in fact, the series of *p*-elements, and the unfilled orbitals 7*d*, 6*f*, 5*g* are filled only afterwards. The structure of the electron shells of atoms at the beginning of the eighth period is as follows:

119	$8s^1$
120	$8s^2$
121	$8s^25g \rightarrow 8s^28p$
122	$8s^25g^2 \rightarrow 8s^28p7d$
123	$8s^25g^3 \rightarrow 8s^28p7d6f$
124	$8s^25g^4 \rightarrow 8s^28p6f^3$
125	$8s^25g^5 \rightarrow 8s^28p5g6f^3$

Of course, this picture of electron distribution in the shells can be a little different. But nevertheless it shows well (and probably quite correctly) the general tendency which is only slightly noticeable in the elements at the beginning of the Periodic system, and which attains its full development in the elements at its very end, at the limit of chemical specificity.

Another manifestation of the same characteristics of electron shells, associated with the downward variations in the groups of the Periodic system, is the growing similarity of energies of separate levels which becomes more appreciable with the increasing atomic number. This can be illustrated by comparing the radii (in 10^{-10} m) of maximum electron densities of neighbouring orbitals, e.g. np and $(n - 1) d$ (the data are based on calculations and taken from Ref. [6]):

E	Ga	In	Tl
n	4	5	6
r_p	1.254	1.382	1.319
r_d	0.275	0.478	0.566
Δr	0.979	0.904	0.753

So, the evolution of the electron shell of the atom (if such a term can only be used to describe the consecutive changes in the atom structure in the Periodic system) consists in upsetting of the initial order of filling of electron orbitals, mutual nearing and mixing of electron shells, which can, in general, be characterized as strengthening of the continuity factor, and respective lessening of the discreteness factor in the atom structure. In other words, a certain “berthollidization” of electron shells can be observed. Using the word “berthollidization” as a metaphor, we should like to emphasize the connection with the general problem of dialectic contradiction in the chemical form of organization of matter [3]. In this particular case, the contradiction between continuity and discreteness shows in the inner contradiction of valency, and in the emergence of new forms of atomic interactions in chemical systems, which even farther deviate from the classical picture of discrete two-centre bond. These cir-

cumstances, which stand out at the microscopic level as a multitude of complicate forms of compounds, are closely connected with and causally depend on the corresponding changes in the electron shells of atoms which manifest as mixing of electron orbitals of different types.

It is possible to state that in the series from the classical interaction H—H to most complicate forms of bond in cluster structures of the transition elements at the "bottom" of the Periodic system, there exists a consecutive transition which is reflected in consecutive changes in the content of the valency concept.

To summarize, it would be expedient to point out a certain analogy in the evolution of the valency concept and the concept of a chemical element. Kedrov, in his book [2], shows that the development of the concept of a chemical element at the first stage is characterized by coexistence of two definitions, *viz.*, chemico-empirical and physico-theoretical. The former is based on purely empirical advances in science. It had been developed outside the atomic theory and related to the pre-Dalton epoch; the latter is based on the Dalton theory. We can also state that the valency concept was formed as an empirical explanation of a topological invariant of the atom. This understanding of valency, as we have already said, brings it near to the empirical parameters of physico-chemical properties. This is why each variation of this concept is associated with a particular series of compounds or types of structure. And this imposes insuperable obstacles to the elaboration of a universal definition of valency.

The theoretical physical definition, which is based on the theory of atomic structure, an independent theoretical foundation, substantiates the physical reality of valency as the property of a free atom. At the same time, the great variety of structures of atomic shells, and particularly of types of interaction in chemical systems, makes it impossible to establish a simple correspondence of a real empirical material (which surpasses theoretical prediction) to the theoretical model, which must serve as a deductive means of description of the entire variability inherent in a given element.

In reality we have a complicate open system of empirical and theoretical views. It is difficult to give a universal definition, while the genetic approach, which reveals the sequence in which the complexity of the valency forms increases, proves to be more fruitful.

References

1. Makarenya, A. A., D. I., *Mendeleev and Physico-chemical Sciences (experiment) of the scientific biography of D. I. Mendeleev*, Atomizdat, Moscow, 1972 (in Russian).
2. Kedrov, B. M., *Evolution of the Concept of Element in Chemistry*, Academy of Sciences Press, Moscow, 1956 (in Russian).

3. Kuznetsov, V. I., *Dialectics of the Development of Chemistry (from history to theory of development of chemistry)*, Nauka, Moscow, 1973 (in Russian).
4. Syrkin, Ya. K., *Periodic system and valency problem*, in book *Centenary of Periodic Law*, Nauka, Moscow, 1969, p. 15-102 (in Russian).
5. Yatsimirsky, K. B., *Complex-formation and Periodic system of elements*, in book *Centenary of Periodic Law*, Nauka, Moscow, 1969, p. 277-283 (in Russian).
6. Shchukarev, S. A., *Inorganic Chemistry*, v. 1, Vysshaya shkola, 1970 (in Russian).
7. Aria, S. M., *Compounds of Variable Composition*, Khimia, Leningrad, 1969, p. 262-325 (in Russian).
8. Korolkov, D. V., *Mendeleev's VKhO*, v. 17, 1972, p. 316-321 (in Russian).
9. Rabinovich, I. V., Telnoi, V. I., Nistratova, V. P., *Transactions of chemistry and chemical technology*, issue 2 (31), Gorky University Press, 1972, p. 12-29 (in Russian).
10. Green, L. H., *The Transition Elements*, vol. 2, Organometallic compounds, by G. E. Coates, M. H. H. Green, K. Wade, London 1968.
11. Fricke, B., Greiner, W., Waber, J., *Theor. Chim. Acta*, 1971, v. 21, p. 235-280.

Molecular-orbital Theory of Valency

The spin-valency theory (see Ch. 5) was the first attempt to interpret the classical concepts of valency as the property of a free atom, and of the chemical bond as pairing of two electrons from the quantum-mechanical standpoint. This theory gives a detailed and comprehensive description of the chemical potentialities of a free atom, but the structural properties of a bound atom are described only in the "ideal pairing" approximation. The electronic structure of a chemical compound is shown here by the only Rumer diagram. This indicates that the spin-valency theory interprets the pre-reaction state of an atom at a new, quantum-mechanical (i.e. not classical) level, while the description of the properties of a bound atom does not extend beyond the limits of the Lewis' theory of electron pairs.

The method of molecular orbitals (MO) is now the main calculation method in quantum chemistry. But its emergence and development did not produce an immediate progress in quantum-chemical interpretation of the classical theory of valency though several facts indicate that the molecular orbitals can successfully be used to define the valency concepts.

First of all, in most cases, the molecular orbitals can be considered as linear combinations of atomic orbitals (the LCAO method). Atomic orbitals depend on the state of the atom, *viz.*, ground, excited, or ionized state. Evidently the atomic orbitals should correspond to those valency potentialities of a free atom which, in the process of transition of this atom into the bound state, are characterized by a certain value, identical or analogous to classical valency. The description of the atom state in a chemical compound becomes especially important in semi-empirical variants of the LCAO method due to a significant dependence of the semi-empirical parameters (atomic potentials of ionization, etc.) on the valency characteristics of atoms.

Secondly, the quantum-chemical calculations are not suitable for the analysis of the hyper-surfaces of potential energy, which determine the interaction of atoms and molecules. Their accuracy is insufficient to predict the structure of chemical compounds and the conditions of chemical reactions. It is therefore reasonable to use the classical theories of valency and chemical structure which are an

inseparable part of modern chemistry and valuable in discussion of its most complicate problems.

Finally, it is necessary to mention that there are various trends in the methods by which the electron structures of chemical compounds are described; these methods use various terms, such as "charge", "population", and bond indices. All these characteristics, provided they are operable, must correspond to the classical theories of valency and chemical structure.

The first definition of the valency concept in the LCAO-MO method was given only in 1972 by Borisova and Semyenov in the USSR [1] and by Armstrong, Perkins, and Steward in England [2]. Their papers were based on the two atomic orbitals bond index given in Ref. [3] (Wiberg index). The molecular-orbital theory of valency was later developed by the same authors [4-6].

The molecular-orbital definition of valency was preceded, both historically and logically, by the determination of chemical bond multiplicity in the terms of the LCAO method. We shall therefore describe the molecular-orbital theory of valency in the same sequence.

1. The Concept of Chemical Bond Multiplicity in the LCAO Method

This paragraph is dedicated to the molecular-orbital definition of multiplicity of the chemical bond between two atoms in a molecule with closed or open electron shells. It is necessary to remember that quantum-chemical formalism, permitting the analysis of the electron structure of a chemical compound in terms of bond multiplicity and atom valencies, implies concrete definitions of the atom bound in a molecule. The formal division of a molecule into separate constituent atoms is not self-evident.

But the concept of atoms which form a molecule has so successfully been used that the rejection of the mathematical formulation of this concept seems reasonable only on the condition that its untenability could convincingly be proved. The introduction of certain quantum-chemical models of the atom in a molecule, whose selection depends on the particular problem to be solved and on considerations of convenience, can be considered reasonable from the physical aspect [7].

With the LCAO method in view, we shall consider the atom A as a certain set of spin orbitals φ_A . There is no doubt that a chemically bound atom cannot be considered to be identical to a free atom [7]. And the set of spin orbitals φ_A , which represents the atom A in a molecule, should not be considered as the spin orbitals φ_A^0 of a free atom A, because these spin orbitals of the atomic nuclei, as they near each other, turn out to be non-orthogonal, and partly incorporate

each other in this sense. Therefore, to work out a mathematical model of a chemically bound atom, we shall use not the atomic spin orbitals φ^0 but the corresponding functions of the ortho-normalized basis. In order that the spin orbitals of free atoms, during orthogonalization of the starting basis

$$\varphi^0 = |\varphi_A^0, \varphi_B^0, \dots| \quad (7.1)$$

could be deformed to the least possible extent, the Löwdin [8] method should preferably be used.

It is shown [1, 6] that the selected spin-orbital model of the atom bound in a molecule makes it possible to compare the classical concept of multiplicity of the chemical bond of two atoms A and B with the quantum-chemical definition:

$$K_{AB} = 2 \sum_{a \in A} \sum_{b \in B} |(S^{1/2} R S^{1/2})_{ab}|^2 \quad (7.2)$$

where $S = \langle \varphi^0 | \varphi^0 \rangle$ is the overlap matrix characterizing the basis φ^0 ; R is the matrix representing the single-electron density in the basis φ^0 (to be more exact, its component corresponding to the maximum value of projection of the full spin momentum of a molecule onto the axis of quantization); a and b are indices of spin orbitals of the atoms A and B.

To prove that quantity K_{AB} , which is determined by the equation (7.2), actually agrees with the classical concept of the chemical bond multiplicity (in the region of its applicability), the following conclusions [1] can be used.

In agreement with the classical concept, the quantity K_{AB} is a material, non-negative value. It is easy to see that the value in question is invariant with respect to the unitary conversions of spin orbitals of any atom in a molecule, i.e. with respect to hybridization and orientation of atomic spin orbitals.

Let columns C_k indicate molecular spin orbitals (MSO) in the basis φ , and the index k enumerate the single-electron states. In the one-determinant version of the LCAO method

$$(S^{1/2} R S^{1/2})_{ab} = \tilde{R}_{ab} = \sum_k C_{ak} C_{bk}^* \quad (7.3)$$

Hence

$$\begin{aligned} K_{AB} &= 2 \sum_{a \in A} \sum_{b \in B} \sum_i \sum_j C_{ai} C_{bi}^* C_{aj}^* C_{bj} = \\ &= \sum_i \sum_j 2 \left(\sum_{a \in A} C_{ai} C_{aj}^* \right) \left(\sum_{b \in B} C_{bi}^* C_{bj} \right) \end{aligned} \quad (7.4)$$

For homonuclear diatomic molecules the molecular spin orbitals can be classified, by their symmetry, into bonding and antibonding. The square matrix of the decomposition coefficients of occupied

molecular spin orbitals into functions φ in virtual MSO can be shown as this:

$$C = \frac{1}{\sqrt{2}} \underbrace{\begin{bmatrix} X & | & X \\ \hline X & | & -X \end{bmatrix}}_{\text{bond antibond}} \frac{A}{B} \quad (7.5)$$

where X is the unitary matrix.

Assuming that bonding spin orbitals are populated in the first instance, so that the number of bonding molecular spin orbitals (n_{bond}) is always greater than that of antibonding spin orbitals (n_{antibond}), it is easy to see that each term in the sum of i and j (7.4) is equal to $1/2$, provided $i = j$, or $-1/2$ if i is bonding and j is antibonding molecular spin orbitals, or vice versa; in all other cases it is equal to zero.

Therefore

$$K_{AB} = (n_{\text{bond}} - n_{\text{antibond}})/2 \quad (7.6)$$

i.e. for homonuclear diatomic molecules, the chemical bond multiplicity is a whole number or half of a whole number, which is equal to a half difference of the number of occupied bonding and antibonding one-electron spin-orbital states.

One-centre unitary conversion of atomic spin orbitals

$$\left. \begin{aligned} \varphi'_A &= \varphi_A X \\ \varphi'_B &= \varphi_B X \end{aligned} \right\} \quad (7.7)$$

rearranges the matrix (7.5) into

$$C' = \frac{1}{\sqrt{2}} \underbrace{\begin{bmatrix} I & | & I \\ \hline I & | & -I \end{bmatrix}}_{\text{bond antibond}} \frac{A}{B} \quad (7.8)$$

where I is a unit matrix.

In other words, atomic spin orbitals of a homonuclear diatomic molecule can be so transformed that the binding molecular spin orbitals will have the form of

$$\psi_{(ab)\text{bond}} = (\varphi'_a + \varphi'_b)/\sqrt{2} \quad (7.9a)$$

and the antibonding will have

$$\psi_{(ab)\text{antibond}} = (\varphi'_a - \varphi'_b)/\sqrt{2} \quad (7.9b)$$

Using the invariability of the density matrix with respect to the unitary transformation of the occupied spin orbitals, part of the latter can be converted into

$$\varphi'_a = (\psi_{(ab)\text{bond}} + \psi_{(ab)\text{antibond}})/\sqrt{2} \quad (7.10a)$$

and

$$\varphi_b' = (\psi_{(ab)\text{bond}} - \psi_{(ab)\text{antibond}})/\sqrt{2}$$

(7.10b)

Thus, part of molecular spin orbitals is equivalent to atomic hybridized and orthogonalized functions while the remaining orbitals, whose number is $(n_{\text{bond}} - n_{\text{antibond}})$, have the form of (7.9a). It follows therefore that *the multiplicity of bond K_{AB} is equal to the number of electron pairs forming the AB bond* (Table 1). It should be noted that the electron spins are not supposed to pair.

In the absence of one-electron spin-orbital interaction, the matrix $\tilde{\mathbf{R}}$, determined by the formula (7.3), has the quasidiagonal form

$$\tilde{\mathbf{R}} = \begin{bmatrix} \mathbf{P}^+ & 0 \\ 0 & \mathbf{P}^- \end{bmatrix}$$

(7.11)

where \mathbf{P}^+ and \mathbf{P}^- are one-electron density matrices, corresponding to the spin momentum projections $+\hbar/2$ and $-\hbar/2$. Taking into account (7.11) which determined K_{AB} , equation (7.2) can be transformed into

$$K_{AB} = \sum_{a \in A} \sum_{b \in B} (|\mathbf{P}_{ab}^+|^2 + |\mathbf{P}_{ab}^-|^2)$$

(7.12)

This quantity can be expressed via matrix elements of electron density

$$\mathbf{P} = \mathbf{P}^+ + \mathbf{P}^-$$

(7.13)

and spin density

$$\mathbf{Q} = \mathbf{P}^+ - \mathbf{P}^-$$

(7.14)

Table 1. Bond Multiplicity in Some Homonuclear Molecules

Molecule	Term	Bond multiplicity	Molecule	Term	Bond multiplicity
H_2^+	$^2\Sigma_g^+$	0.5	C_2	$^1\Sigma_g^+, ^3\Pi_u$	2
H_2	$^1\Sigma_g^+$	1	N_2^+	$^2\Sigma_g^+$	2.5
He_2^+	$^2\Sigma_u^+$	0.5	N_2	$^1\Sigma_g^+$	3
He_2		0	O_2^+	$^2\Pi_g$	2.5
Li_2	$^1\Sigma_g^+$	1	O_2	$^3\Sigma_g^-$	2
Be_2		0	F_2	$^1\Sigma_g^+$	1
B_2	$^3\Sigma_g^-$	1			

as follows:

$$K_{AB} = \sum_{a \in A} \sum_{b \in B} (|P_{ab}|^2 + |Q_{ab}|^2) \quad (7.15)$$

The first member in the right-hand part of this sum is the Weberg index. It is used to characterize chemical bonds in molecules with closed electron shells, provided their structure is calculated by the zero approximation of differential overlapping [3].

In diatomic heteronuclear molecules, the basis atom functions are

$$\psi_{(ab)} = C'_a \varphi'_a \pm C'_b \varphi'_b, \quad |C'_a| > |C'_b| \quad (7.16)$$

Therefore, the molecular spin orbital of the type (7.16) is intermediate between a strictly two-centre MSO (7.9a) or (7.9b) of a homonuclear diatomic molecule and the atomic function φ'_a . And hence multiplicity of chemical (covalent) bond in a heteronuclear diatomic molecule is less than in a homonuclear molecule isoelectronic to it.

For example, for the isoelectronic series N_2 , CO, BF, bond multiplicity markedly decreases with the increasing difference between the atomic numbers of bound atoms (Table 2). In a molecule of N_2 , a strictly covalent triple bond is formed by one molecular orbital of the σ -type and two MO of the π -type, while in a molecule of CO, and especially in a molecule of BF, this bond is polarized so that molecular orbitals (and first of all molecular orbitals of the π -type) are located in the vicinity of oxygen or fluorine nuclei and preserve, to a considerable degree, the character of the orbitals of unshared electron pairs of these atoms. But partial delocalization of ele-

Table 2. Bond Multiplicity in N_2 , CO, and BF Molecules

Molecule	Bond multiplicity	σ - and π -constituents of bond multiplicity
N_2	3	$\sigma: 1, \pi: 1+1$
CO	2.66	$\sigma: 0.93, \pi: 0.87 \times 2$
BF	1.50	$\sigma: 0.70, \pi: 0.40 \times 2$

Table 3. Atom Charge and Bond Multiplicity of Hydrogen Halide Molecules

Molecule	q_H	q_{Hal}	K
HF	+0.35	-0.35	0.88
HCl	+0.12	-0.12	0.99
HBr	+0.07	-0.07	1.00

electron pairs into the bond region is responsible for the fractional multiplicity of the bonds in CO and BF molecules.

The HF, HCl, and HBr molecules are, strictly speaking, not isoelectronic but the number of valency electrons, which determine the character of bond and its multiplicity, is equal in them. The bond is formed by only two atomic orbitals: 1s-orbital of hydrogen and valency hybrid σ -orbital of the halogen. The halogen also has the inner electron shells and three unshared electron pairs in the valency shell (one σ - and two π -types). Multiplicity of the hydrogen-halogen bond in the series HBr, HCl, and HF decreases with increasing polarity* (Table 3).

Thus, the quantum-chemical determination of multiplicity of chemical bonds proves useful in the discussion of even relatively simple heteronuclear diatomic molecules. Further we shall give more complicated examples of molecular-orbital calculations of valency structures of polyatomic molecules, which extend beyond the scope of the classical theory of valency.

2. Quantum-chemical Interpretation of Valency

A certain valency, which is understood as a quantity characterizing the state of a given atom in a molecule, is ascribed by the classical theory of chemical structure to each atom bound in a molecule. For example, carbon is considered to be tetravalent in CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , trivalent in CH_3 , divalent in CH_2 , and monovalent in CH ; chlorine is monovalent in HCl , Cl_2 , ClF , trivalent in ClF_3 , and penta valent in ClF_5 , etc. Distribution of the valency of atom A (V_A) by its bonds with other atoms in a given chemical compound is described by bond multiplicity K_{AB} , according to this equation (see, e.g. [9]):

$$V_A = \sum_{B(\neq A)} K_{AB} \quad (7.17)$$

Substituting (7.2) in this equation we determine valency V_A through \mathbf{R} and \mathbf{S} :

$$V_A = 2 \sum_{a \in A} \{ (\mathbf{S}^{1/2} \mathbf{R} \mathbf{S} \mathbf{R} \mathbf{S}^{1/2})_{aa} - \sum_{a' \in A} |(\mathbf{S}^{1/2} \mathbf{R} \mathbf{S}^{1/2})_{aa'}|^2 \} \quad (7.18)$$

As shown in [1], the unitary conversion (hybridization) of atomic spin orbitals

$$\chi_a^0 = \sum_{\bar{a} \in A} \varphi_{\bar{a}}^0 U_{a\bar{a}}^{(A)}; \quad a, \bar{a} \in A \quad (7.19)$$

* A semi-empirical version of the LCAO method offered by Hoffman was used to calculate valency structure of the hydrogen halide molecules. The method takes into account atomic charges q_{H} and q_{halogen} .

simplifies the expression (7.18) as this:

$$V_A = 2 \sum_{\bar{a} \in A} \{ (S^{1/2} \mathbf{R} S^{1/2})_{\bar{a}\bar{a}} - |(S^{1/2} \mathbf{R} S^{1/2})_{\bar{a}\bar{a}}|^2 \} \quad (7.20)$$

Each spin orbital ψ_k can be characterized by compactness, i.e. an average (in the quantum-mechanical sense) number of electrons in the one-electron state described by a given spin orbital

$$\lambda_k = \langle \psi_k | \hat{\rho} | \psi_k \rangle \quad (7.21)$$

and by a square of dispersion (mean quadratic fluctuation) of the number of electrons in this state

$$(\Delta \lambda_k)^2 = \langle \psi_k | (\hat{\rho} - \lambda_k)^2 | \psi_k \rangle = [\langle \psi_k | \hat{\rho}^2 | \psi_k \rangle - \lambda_k^2] \quad (7.22)$$

The one-electron density operator $\hat{\rho}$ is represented by a one-electron matrix of density, which determines the state of a many-electron system with respect to the values in question which have the corresponding one-electron operators*.

Assuming that

$$\psi_k = \sum_l \chi_l^0 (\bar{S}^{-1/2})_{lk} \quad (7.23)$$

where

$$\bar{S} = \langle \chi^0 | \chi^0 \rangle \quad (7.24)$$

and comparing formulas (VII.20) and (VII.22) we obtain the equation

$$V_A = 2 \sum_{\bar{a} \in A} (\Delta \lambda_{\bar{a}})^2 \quad (7.25)$$

which discloses the quantum-chemical concept of valency. *The valency of an atom is equal to a doubled sum of squares of population dispersion of hybridized and orthogonalized spin orbitals representing this atom in a given chemical compound.* This interesting result is reported in work [5].

It should be noted that the sum

$$\lambda_A = \sum_{a \in A} \lambda_a \quad (7.26)$$

determines the full electron population of the atom A. This quantity is often replaced by the formal charge on the atom

$$q_A = Z_A - \lambda_A \quad (7.27)$$

where Z_A is the charge on the atom nucleus.

* The operator $\hat{\rho}$ characterizes the state of the system but it is not an operator of any observed value.

The formal charge of the atom, probably, corresponds to its electrovalency.

To illustrate this formalism, consider a few examples of quantum-chemical studies of the valency structure of chemical compounds.

Valency of atoms in homonuclear diatomic molecules is expressed by a whole number or its half and coincides with the bond multiplicity in these molecules (Table 1).

Valency structure of molecule HCN. The calculated parameters of the valency structure of HCN practically coincide with those ascribed to this molecule by classical theory: ordinary bond H—C and triple bond C≡N, monovalent hydrogen, tetravalent carbon and trivalent nitrogen (Table 4).

Simplest hydrides. The correspondence of the formalism and the concepts of the classical theory of chemical structure (in the field of application of the latter) is confirmed by quantum-chemical calculations of valencies of atoms and bond multiplicities in hydrides having the composition AH_k. We accomplished these calculations using molecular orbitals determined by the Hoffman method with

Table 4. Valency Structure of HCN Molecule

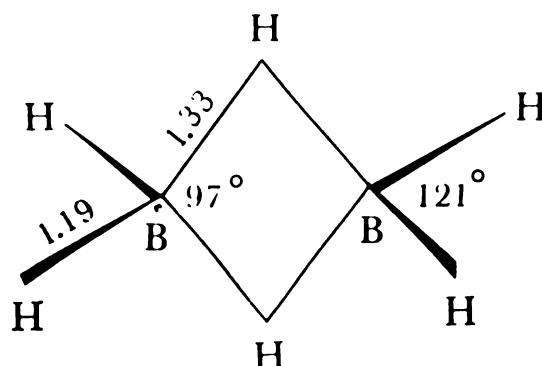
Element	Valency	Bond	Multiplicity
H	1.0	HC	1.0
C	4.0	CN	3.0
N	3.0	HN	0.0

Table 5. Atom Valencies and Bond Multiplicities in EH_k Hydrides

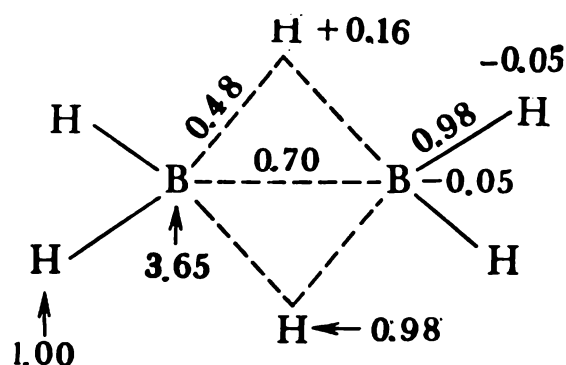
EH _k	V _E	V _H	K _{EH}	K _{HH}
LiH	0.86	0.86	0.86	
(BeH ₂)	1.98	0.99	0.99	0.00
(BH ₃)	3.00	1.00	1.00	0.00
CH ₄	3.98	1.00	1.00	0.00
NH ₃	2.88	0.99	0.96	0.02
OH ₂	1.96	0.98	0.98	0.00
FH	0.88	0.88	0.88	
ClH	0.99	0.99	0.99	
BH ₄ ⁻	3.89	0.97	0.97	0.00
CH	0.99	0.99	0.99	
CH ₂	1.97	0.99	0.98	0.01

self-adjustment by formal charges of atom.* The results given in Table 5 indicate that the valency of hydrogen in hydrides is close to unity and can therefore be used as a standard for the determination of valencies of the other elements. And actually, the valency of the element A in hydrides AH_k is close to the number of the attached hydrogen atoms (k).

Boron hydride molecule. The structure of the molecule of boron hydride (diborane)



is very interesting from the point of view of the valency theory because two hydrogen atoms (H') of this molecule are bonded with two equidistant neighbouring boron atoms (B), while boron atoms are connected directly with four hydrogen atoms. It is also possible that boron atoms are bonded. It is interesting therefore to give a quantum-chemical analysis to the diborane molecule structure. The results of the analysis are given in this diagram:

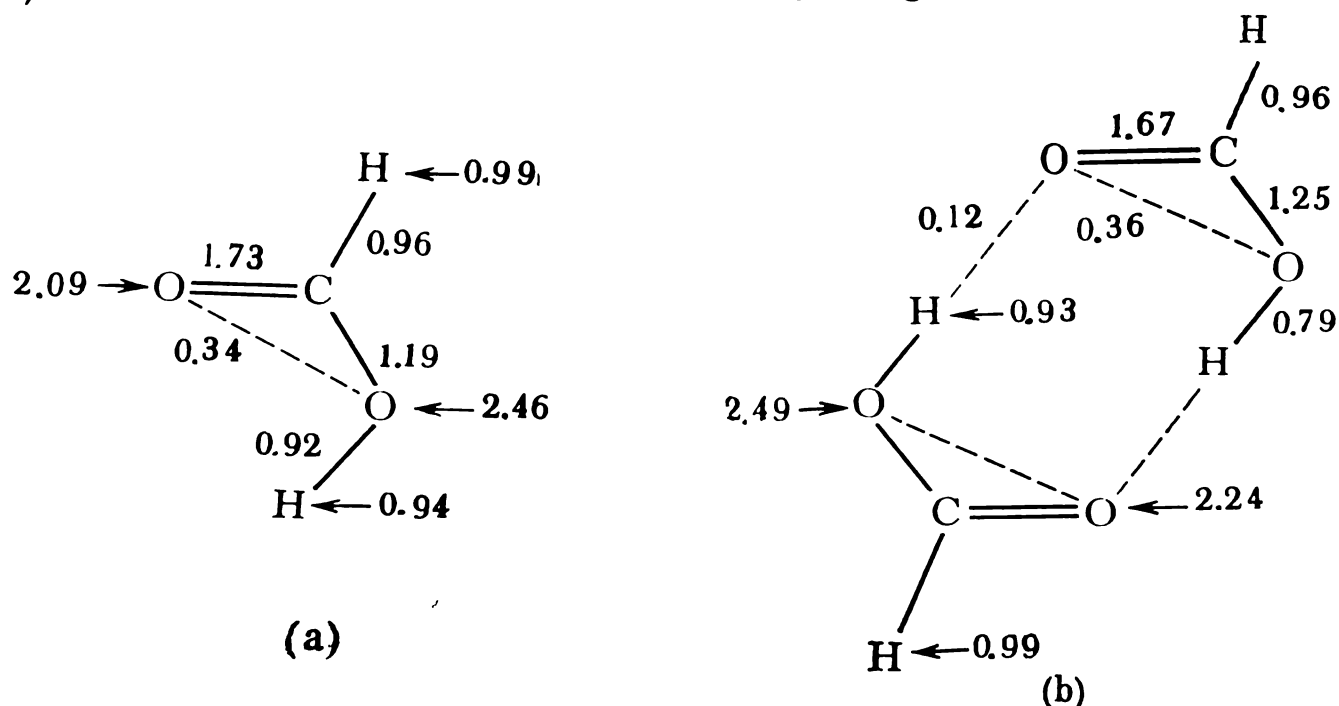


Bond multiplicities are indicated over the corresponding valency dashes, valencies are subscribed under the arrows directed to the atoms, and formal charges are designated by numbers with the appropriate signs.

Hydrogen bond in the dimer of formic acid $(HCO_2H)_2$. Valencies of atoms and multiplicities of bonds in the monomer (a) and dimer

* We used this method in our further calculations, the results of which are given below.

(b) of formic acid are shown in valency diagrams:

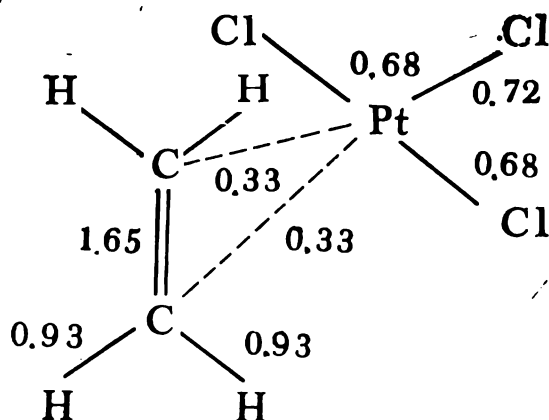


It is interesting to note that the valency of hydrogen atoms involved in the formation of the hydrogen bond does not increase during association, but the valency of oxygen atoms in the hydrogen bridge increases significantly. Quantum-chemical calculations show that these effects are observed in other compounds with hydrogen bonding.

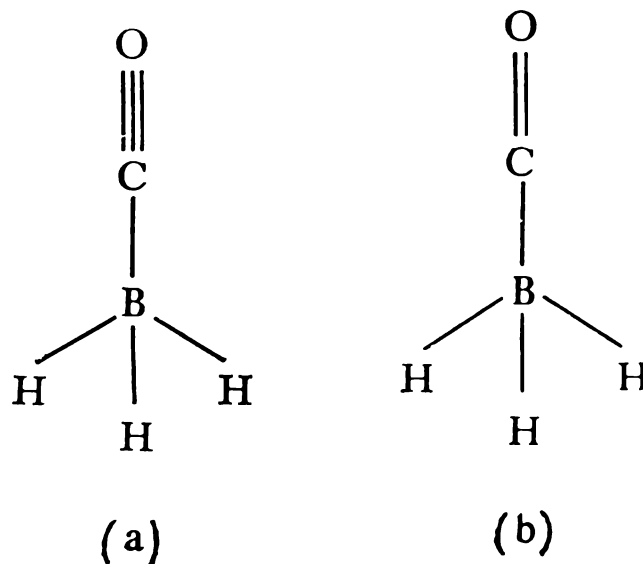
Zeise salt. The quantum-chemical calculation of the valent structure of the platinum chloride complex $[\text{C}_2\text{H}_4\text{PtCl}_3]^-$, which extends beyond the limits of the classical theory of valency, was performed by Armstrong, Fortune, and Perkins [10]. According to this calculation, the valencies of the atoms in the Zeise salt have the following values:

Atom	Pt	C	H	<i>cis</i> -Cl	<i>trans</i> -Cl
Valency	2.9	4.0	1.0	1.1	1.2

The distribution of valencies by the bonds is described by their multiplicities:



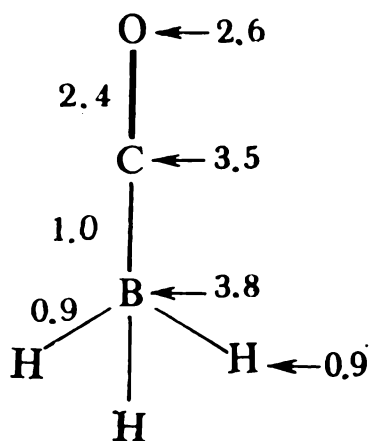
Carbonyl borohydride. The structure of the carbonyl borohydride H_3BCO molecule (C_{3v} symmetry) was considered by Tatevskii [9]. As he analysed experimental data concerning carbonyl borohydride structure and compared the interatomic distances r_{BH} , r_{HC} , r_{HO} , r_{BC} , and r_{CO} with the corresponding interatomic distances in the molecules of BH , $\text{B}(\text{CH}_3)_3$, CO , H_2CO , HFCO , F_2CO , Cl_2CO , FCICO , Tatevskii arrived at a conclusion that the structure of the H_3BCO molecule can be described in the classical theory by two structural formulas:



The atoms of boron and oxygen (a) or the atoms of boron and carbon (b) are given unusual valencies here:

$$V_{\text{B}} = 4, V_{\text{O}} = 3 \text{ or } V_{\text{B}} = 4, V_{\text{C}} = 3.$$

The molecular-orbital calculation made by Armstrong, Stewart, and Perkins [4] removes variations in the description of the carbonyl borohydride valency structure:



Multiplicities of chemical bonds are given at the left, and atom valencies at the right. The results of the calculation indicate that the valency structure of carbonyl borohydride is intermediate between two structures offered by Tatevskii.

A systematic quantum-chemical investigation of the valency of atoms from hydrogen to chlorine by the LCAO method in the approximation of complete neglect of the differential overlapping was made in works [2] and [4]. Thus it is shown in Ref. [4], that the valency of lithium, beryllium, and boron, with proper consideration of the structure of compounds of these elements, is much higher than the corresponding number of the group of the Periodic system.

Interesting results have been obtained for fluorides of phosphorus, sulphur, and chlorine. The valency of these elements turns to be close to the number of fluorine atoms which are attached to them (though the bonds in these compounds, characterized by excess quantities of electrons, are markedly delocalized: valency V_P in PF_5 is 4.94; V_S in SF_6 is 5.92; V_{Cl} in ClF is 1.22, in ClF_3 it is 3.05, and in ClF_5 it is 4.78. It should be noted that the results obtained by the authors of works [2, 4] for molecules with open electron shells are, in our opinion, erroneous. For example, according to the formalism of the paper [2], the molecular ion H_2^+ is characterized by the multiplicity of bond (Wiberg index) of $K = 0.25$ and the valency $V_H = 0.75$, and the molecule of O_2 is characterized by $K = 1$ and $V_O = 2.5$, etc. (cf. Table 1). And the equality of valency to the sum of multiplicities, which is the principle of this paper, becomes upset. The formalism of the paper [2] does not take into account the overlapping of atomic orbitals, nor does it extend beyond the limits of the zero differential overlap approximation.

The valency of elements whose atoms have vacant d -electron shells is of special interest. Armstrong, Fortune, and Perkins [10] used the molecular orbital method to calculate the valency of platinum in its complex ions, *trans*- $[PtXCl_3]$ and *trans*- $[PtX(NH_3)Cl_2]$ (where X are C_2H_4 , PH_3 , CO , H_2S , NH_3 , H_2O , H^- , CN^- , CH_3^- , Br^- , Cl^- , OH^- , NO_2^-). They discovered that the valency of platinum in these compounds varies within the range of $2 < V_{Pt} < 3$.

A more detailed investigation of the valency structure of platinum complexes was carried out by Sizova and Baranovskii [11]. They extended the concept of atom valency to polyatomic ligands (L) and characterized their σ - and π -donating (or accepting) power with σ - and π -constituents of valency V_L to classify eleven most important ligands according to their donating and accepting properties. They considered the dependence of the ligand properties on the composition of the complex and studied the mutual influence of the ligands, effected through the platinum orbitals. Sizova and Baranovskii also established that chemical bond can be formed between ligands in the *cis*-position. In some cases this direct interaction of the ligands can be very important for the explanation of the nature of the *cis*-effect while the static *trans*-effect is mainly determined by the interaction through the central atom and depends on the electron-donating characteristics of the ligand.

3. Valency Structure of Organic Compounds

The quantum-chemical calculations of valency structures of organic compounds based on the formalism mentioned in the previous paragraph agree with the fundamental postulate of the classical theory of chemical structure, viz., tetravalency of carbon in stable organic compounds. Multiplicities of the carbon-carbon bonds, characteristic of these compounds, vary within a sufficiently wide range. Along with ordinary, double and triple bonds, it is possible to distinguish bonds with intermediate multiplicity in conjugated compounds. Calculation of parameters of the valency structure in these compounds helps conclude on the chemical properties of these compounds.

Simplest hydrocarbons. Formal charges, valencies of atoms, and multiplicities of bonds in the simplest (isolated) hydrocarbons are given in Table 6. Multiplicity of the carbon-carbon bond in ethane, ethylene, and acetylene is expressed by whole numbers which is explained by its non-polar and localized character in these compounds.

In the series ethane-ethylene-acetylene, the carbon-hydrogen bond multiplicity decreases and its ionicity increases with growing acidity [2].

Benzene molecule. The valency structure of a benzene molecule is a regular hexagon of tetravalent ($V_C = 3.99$) carbon atoms each of which is bound with two neighbours by a bond, whose multiplicity K_{CC} is 1.44; with the opposite carbon atom by a bond whose multiplicity is 0.12; and with the adjacent hydrogen atom by a bond which is almost ordinary. It can be indicated that these parameters of the benzene valency structure agree with the commonly accepted opinion and verify it.

Pyridine molecule and pyridinium ion. The valency structure of pyridine (Tables 7 and 8) is very much like that of benzene. And its chemical properties have the same marked aromaticity. What differs pyridine from benzene is the presence of a trivalent ($V_N = 3.0$) nitrogen atom in the aromatic six-membered ring, the nitrogen

Table 6. Formal Charges (q), Valencies (V) of Atoms, and Multiplicities (K) of Bonds of Adjacent Atoms in Simplest Hydrocarbons

Molecule	q_C	q_H	V_C	V_H	K_{CH}	K_{CC}
CH_4	-0.20	+0.05	3.98	0.997	0.996	
H_3C-CH_3	-0.16	+0.05	3.98	0.997	0.992	1.00
$H_2C=CH_2$	-0.13	+0.065	3.99	0.996	0.986	2.01
$HC\equiv CH$	-0.12	+0.12	3.97	0.986	0.962	3.00

atom having an unshared electron pair of the σ -type (to be more exact, a fully symmetrical hybrid atomic orbital with the population of 1.97). This circumstance determines the basic properties of pyridine as a cyclic tertiary amine which attaches a proton in an acid medium to form a pyridinium ion. The charge of the proton which penetrates into the region of localization of the nitrogen atom unshared electron pair is distributed in the σ -system and it polarizes the π -system of the pyridinium ion; π -electrons of the aromatic ring are displaced towards nitrogen, which, in the pyridinium ion, carries the positive formal charge. The alternation of bond multiplicity in pyridinium is more marked than in pyridine (Tables 8 and 9). Nevertheless the valency structure is not strongly distorted during protonization of pyridine and hence the pyridinium ion retains the aromatic properties of pyridine.

Table 7. Formal Charges (q), Valencies (V) of Atoms, and π -Electron Population (λ_π) in the Pyridine Molecule and Pyridinium Ion

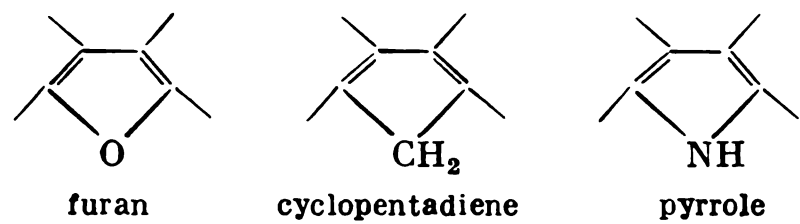
Atoms	q_H		V		λ_π	
	C_5H_5N	$C_5H_5NH^+$	C_5H_5N	$C_5H_5NH^+$	C_5H_5N	$C_5H_5NH^+$
N	-0.11	+0.14	3.03	3.71	1.16	1.45
C ₁	-0.05	+0.04	3.98	3.96	0.96	0.89
C ₂	-0.07	-0.02	3.99	3.98	0.99	0.95
C ₃	-0.06	-0.01	3.98	3.97	0.95	0.88
H ₁	+0.07	+0.12	0.995	0.986		
H ₂	+0.08	+0.10	0.994	0.989		
H ₃	+0.11	+0.13	0.988	0.983		
H _N		+0.24		0.942		

Table 8. Bond Multiplicities in Pyridine Molecule *

Atoms	C ₁	C ₂	C ₃	C ₄	C ₅	H ₁	H ₂	H ₃	H ₄	H ₅
N	1.42	0.02	0.12	0.02	1.42	—	—	—	—	—
C ₁		1.44	—	0.11	—	0.98	—	—	—	—
C ₂			1.43	—	0.11	—	0.98	—	—	—
C ₃				1.43	—	—	—	0.98	—	—
C ₄					1.44	—	—	—	0.98	—
C ₅						—	—	—	—	0.98

* In this and other tables, which follow, values of $K < 0.01$ are designated by a dash.

Pyrrole and furan molecules. The molecules of pyrrole and furan can formally be obtained by substituting the NH group and an oxygen atom respectively for the CH₂ group in a conjugated system of cyclopentadiene having four π -electrons and showing no aromatic properties:



Nitrogen or oxygen must form two σ -bonds. If their formal charges are preserved, there must be an unshared electron pair of the π -type (oxygen atom must have an unshared electron pair of the σ -type as well). The π -electron systems of pyrrole and furan are thus a sextet of electrons, and this circumstance indicates that pyrrole and furan may probably have aromatic properties. But this probability

Table 9. Bond Multiplicities in the Pyridinium Ion

Atoms	C ₁	C ₂	C ₃	C ₄	C ₅	H ₁	H ₂	H ₃	H ₄	H ₅	H _N
N	1.34	—	0.08	—	1.34	—	—	—	—	—	0.92
C ₁		1.45	0.03	0.11	0.05	0.97	—	—	—	—	—
C ₂			1.42	—	0.11	—	0.97	—	—	—	—
C ₃				1.42	0.03	—	—	0.97	—	—	—
C ₄					1.45	—	—	—	0.97	—	—
C ₅						—	—	—	—	0.97	—

Table 10. Formal Charges (*q*), Valencies (*V*) of Atoms and π -Electron Population (λ_π) in Pyrrole and Furan Molecules

Atoms	<i>q</i>		<i>V</i>		λ_π	
	C ₄ H ₄ NH	C ₄ H ₄ O	C ₄ H ₄ NH	C ₄ H ₄ O	C ₄ H ₄ NH	C ₄ H ₄ O
N/O	+0.01	−0.00	3.54	2.56	1.64	1.61
C ₁	−0.08	−0.05	3.96	3.91	1.08	1.13
C ₂	−0.13	−0.10	3.98	3.98	1.10	1.06
H ₁	+0.07	+0.09	0.995	0.992	—	—
H ₂	+0.05	+0.06	0.998	0.996	—	—
H _N	+0.16	—	0.974	—	—	—

is realized only on the condition that the π -electron pair is delocalized by the five-membered cycle*.

The results of calculation of the valency structure of pyrrole and furan molecules are given in Tables 10, 11, 12. They confirm delocalization of the π -electron pair of heteroatom in these molecules. But the positive charge on the heteroatom, which is the result of this delocalization, is compensated for by the electrons of the σ -system.

Tables 11 and 12 show that the alternation of multiplicities of the carbon-carbon bonds in pyrrole and furan molecules is great. Their aromatic properties are therefore weaker than in benzene or pyridine. While comparing the valency structures of pyrrole and furan, one can expect that furan, which is characterized by a greater alternation of multiplicities of the carbon-carbon bond will have weaker aromatic and stronger diene properties. And this is actually so. In contrast to pyrrole and other aromatic compounds, furan readily enters into reactions of 1,4-addition to give adducts with active dienophiles.

C₃ and H₂C₃H₂ molecules. The valency states of the central and the marginal atoms of carbon in a linear molecule of C₃ are different. The central carbon atom is tetravalent ($V = 3.97$), while the mar-

Table 11. Bond Multiplicities in the Pyrrole Molecule

Atoms	C ₁	C ₂	C ₃	C ₄	H ₁	H ₂	H ₃	H ₄	H _N
N	1.21	0.07	0.07	1.21	—	—	—	—	0.965
C ₁		1.61	0.01	0.14	0.98	—	—	—	—
C ₂			1.28	0.01	—	0.98	—	—	—
C ₃				1.61	—	—	0.98	—	—
C ₄					—	—	—	0.98	—

Table 12. Bond Multiplicities in the Furan Molecule

Atoms	C ₁	C ₂	C ₃	C ₄	H ₁	H ₂	H ₃	H ₄
O	1.17	0.10	0.10	1.17	—	—	—	—
C ₁		1.64	—	0.11	0.97	—	—	—
C ₂			1.24	—	—	0.98	—	—
C ₃				1.64	—	—	0.98	—
C ₄					—	—	—	0.97

* The nitrogen atom must, in this case, lose its nucleophilic (or basic) properties.

ginal atoms have lower valency (2.58). The central atom is connected with each marginal atom by a double bond ($K = 1.98$).

A molecule of allene can formally be obtained by adding two hydrogen atoms to each marginal carbon so that the plane of one CH_2 group would be perpendicular to the plane of the other group. The valency of the central carbon atom remains 3.97; the multiplicity of its bonds with the neighbouring carbon atoms is 1.97, but the valency of the marginal carbon atoms increases to 3.98. It is important to note that multiplicity of the direct bond of the marginal carbon atoms is considerable (0.60) in the C_3 molecule; but it almost completely disappears (0.05) in allene. This indicates that two-centre bonds in allene are more localized than in the C_3 molecule.

Butadiene molecule in the ground and first excited states. The calculation of the valency structure of the butadiene molecule in the ground singlet, and in the first excited triplet state gives the results summarized in Tables 13 and 14.

The tabulated data indicate that the spin density in the triplet state is concentrated at the terminal carbon atoms. Multiplicity of the central carbon-carbon bond greatly increases in the considered excited state and the multiplicity of the marginal bonds simultaneous-

Table 13. Formal Charges, Spin Population, and Atom Valencies in a Molecule of Butadiene for Singlet ($S=0$) and Triplet ($S=1$) States

State	Atom	Charge	Spin population	Valency
$S=0$	C_1	-0.12	0	3.99
	C_2	-0.09	0	3.98
	H	$+0.07$	0	0.995
$S=1$	C_1	-0.13	0.69	3.51
	C_2	-0.08	0.31	3.90
	H	$+0.07$	0	0.995

Table 14. Multiplicities of Carbon-carbon Bonds in the Butadiene Molecule for a Singlet ($S=0$) and a Triplet ($S=1$) State

State	$S=0$			$S=1$		
Atoms	C_2	C_3	C_4	C_2	C_3	C_4
C_1	1.86	0.01	0.15	1.23	0.22	0.10
C_2		1.13	0.01		1.47	0.22
C_3			1.86			1.23

ly decreases with the result that the former exceeds the latter. The first circumstance indicates the high reactivity of the terminal carbon atoms in the radical-type reactions, and the second shows that the central bond in the triplet state of butadiene must be shorter than the others. This was not predicted but use was made of the ground state geometry.

4. Conclusion

The theory discussed in this chapter is the first and, by now, the only quantum-chemical theory of valency. It is formulated on the basis of the LCAO method and agrees with the classical concept of valency. The main point from which the theory starts is the molecular-orbital determination of multiplicity of covalent chemical bonds in terms of the density matrix and atomic orbital overlapping matrix. The atom valency, which is understood as a value characterizing the state of an atom in a chemical compound, is determined by summation of multiplicities of bonds of a given atom with the other atoms in a chemical compound. This definition reveals the connection of the atom valency with the quantum-chemical indefiniteness (to be more exact, mean-quadratic fluctuation) of its hybrid orbital population.

The agreement of the quantum-chemical definitions with the classical theory of valency has been demonstrated by the analysis of the valency structure of homonuclear diatomic molecules, hydrides having the composition EH_k , molecules of hydrogen cyanide, and simplest hydrocarbons. Discussed were some organic molecules, such as benzene and aromatic heterocycles, which are characterized by delocalization of two-centre chemical bonds, and hence their fractional multiplicity. The existence of the latter was proved before the establishment of quantum mechanics. The molecular-orbital theory of valency makes it possible to calculate fractional multiplicities of the carbon-carbon and carbon-heteroatom bonds, and at the same time it confirms Kekulé's postulate of tetravalency of carbon in its stable compounds.

The molecular-orbital theory of valency can be used to establish the valency structure of compounds which cannot be explained by the classical theory of valency. These are, for example, diborane, dimer of formic acid, Zeise salt, carbonyl borohydride. The studies of real structures of chemical substances, which have been carried out in the past decades, show that most inorganic compounds should be considered "non-classical" because, due to delocalization and polarization of chemical bonds, the valency of their atoms and multiplicities of their bonds cannot be characterized by whole numbers.

References

1. Borisova, N. P., Semenov, S. G., *Trans. of Leningrad University*, 1973, No. 16, p. 119-124 (in Russian).
2. Armstrong, D. R., Perkins, P. G., Stewart, J. J. P., *J. Chem. Soc.*, 1973, p. 838-840.
3. Wiberg, K. B., *Tetrahedron*, 1968, v. 25, p. 1083-1096.
4. Armstrong, D. R., Perkins, P. G., Stewart, J. J. P., *J. Chem. Soc.*, 1973, p. 2273-2277.
5. Borisova, N. P., Semenov, S. G., in book "Quantum Chemistry", Kishinev, "Shtiintsa", 1975, p. 26-31 (in Russian).
6. Borisova, N. P., Semenov, S. G., *Trans. of Leningrad University*, 1976, No. 16, p. 98-103 (in Russian).
7. Ruedenberg, K., *Physical Nature of Chemical Bond*, Rev. Mod. Physics, vol. 34, No. 2, 1962, p. 2-167.
8. Löwdin, P., *Adv. in Quant. Chem.*, 1970, v. 5, p. 185-199.
9. Tatevskii, V. M., *Classical Theory of Molecular Structure and Quantum Mechanics*, Moscow, Khimia, 1973 (in Russian).
10. Armstrong, D. R., Fortune, R., Perkins, P. G., *Inorganica chim. Acta*, 1974, v. 9, p. 9-18.
11. Sizova, O. V., Baranovskii, V. I., *Theoretical and Experimental Chemistry*, 1975, v. 11, p. 147-155 (in Russian).

Dynamic and Cooperative Processes of Electron Density Redistribution and the Valency Problem

The development of modern theoretical chemistry is based mainly on the intense use of physical methods. The physical structural methods (especially radiospectroscopic ones) are very sensitive to the structural changes in molecules caused by external fields and reagents. They can be used for the experimental studies of intimate processes of the electron and nucleus density distribution in both space and time. The modern synthetic chemist cannot limit himself, for example, to the idea of static charge or static valency, but must adapt himself to new categories in modern quantum chemistry, physics, and static physics. The novelty of these ideas is, to a considerable degree, connected with electron and nuclear dynamics, with time dependence of micro-processes lasting for 10^{-4} to 10^{-16} sec. Moreover, synthetic chemistry effectively uses today the tunnel and tunnel-activating processes, and also coherent processes, which allow to act on certain electron and vibration transitions and make the molecular system several orders more reactive.

The development of quantum mechanics has introduced into theoretical chemistry the concepts of localization and delocalization of micro-particles, and of the characteristic time of measurement. In 1927, Hund [1] used quantum mechanics and the idea of leakage through the potential barrier to formulate the problem of possible existence of several energetically equivalent configurations in polyatomic molecules. This work precedes the study of electron tunneling in metals [2, 3] as well as the explanation of radioactive decay [4]. Hund's hypothesis on the tunnel splitting has been proved experimentally by micro-wave absorption spectra of an ammonia molecule. We now understand this process in terms of the Jahn-Teller theorem [5] which has been applied during the past two decades to many inorganic and organic molecules [6, 10, 11].

For a symmetrical double-well system it is important to know in which well a particle is present at a given moment of time (the characteristic time of an external field or a detector). If the method registers one of the states with a localized particle, one can speak about localization in the dynamic or quasistationary sense. If in the lapse of the resolution time the particle performs several quantum-

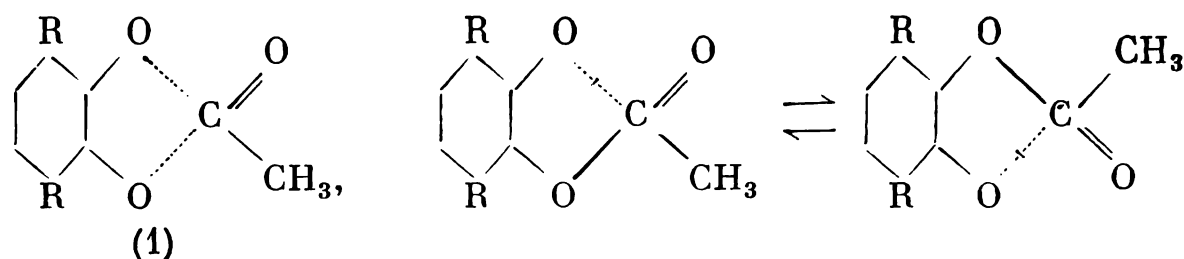
mechanical vibrations, the stationary state or delocalization must be observed [7-9].

In the absence of one state, it is possible to speak about an unrigid configuration of a molecule and, accordingly, about unrigid point symmetry groups by which unrigid molecules are now classified [11-15]. A nitrogen atom in ammonia has two equilibrium positions, *viz.*, above and beneath the plane formed by three hydrogen atoms. The unrigid point group of the ammonia molecule D_{3h} has more symmetry elements than the rigid point group C_{3v} which describes a pyramidal structure.

Complicated molecular systems can, naturally, have a complicated potential surface with many minima, and the character of this surface depends on the parameters of a concrete system in the ground and excited states. For instance, an octahedral particle with the central atom can undergo tetragonal deformation (the octahedron turns into an elongated or a compressed tetragonal bipyramid), rhombic deformation (the octahedron turns into a rhombic bipyramid), trigonal deformation (the octahedron turns into a trigonal rhombohedron), etc. Any molecules having similar nuclei can, in principle, have several spatial surface configurations differing in nuclei transposition, provided these re-orientations are not equivalent to the rotation of a molecule as a whole.

The works of the past few years provide many examples of the manifestation of complex intramolecular nuclei movements in compounds of various types. Resonance methods, such as NMR, EPR, and the phonon scattering method, can be used to investigate quantitatively the keto-enol tautomerization and intramolecular migration of organic fragments in β -diketone derivatives. The tunnel tautomeric low-temperature transference of the groups F^- , OH^- , CN^- was proved by measuring heat conductivity in defective structures of alkali metal halides [16]. The tunnel and activation processes are always associated with high nuclear displacement when periodic internal re-orientations of separate atoms or whole molecular fragments occur in a molecule. Such transitions and "the movements with a large amplitude" are called stereochemically unrigid [15]. All these new ideas must be logically supplemented with the concept of dynamic charge (valency) on the atomic centre in the molecule. During the tunnel or tunnel-activating vibrations, the changes in the molecule geometry cause the appropriate change in the effective charge or electron density in certain regions of a molecular system or on the atomic centres. The reactivity of a certain centre in a molecule, which performs quantum-mechanical vibrations, depends on the effective charge on the centre and the geometry of this molecule at a given moment of time. The nitrogen atom in an ammonia molecule, and its unshared electron pair are open to the attack by the reagent having its characteristic time only at cer-

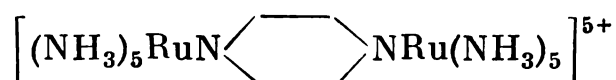
tain moments of time. The changes in the electron and spin density on the atomic centres in the process of dynamic re-arrangement become clearly visible in the EPR spectra [17]:



The removal of quasi-degeneration in the structure (Jahn-Teller effect) (1) results in two equivalent states with displacement of an unpaired electron from one oxygen atom onto another.

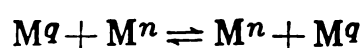
In some cases, the dynamic charge (or energy state) in the tunnel-activating bonds (in bonds with the atom transfer along the chemical bond line) can be shown schematically by circles, as e.g. in works [19-21]. The hydrogen atom in the hydrogen bond can have two positions $O \cdots \underset{\circ}{\underset{\circ}{H}} - O$ [18]; the same picture is with fluorine atom in the bridge $Sn \cdots \underset{\circ}{\underset{\circ}{F}} - Sn$ in $[(CH_3)_3SnF]_\infty$ [19]; the beryllium atom in $(C_5H_5)_2Be$ [20]. It is necessary to emphasize again that the interpretation of the resonance methods spectra and other physical properties [15] should be based on the classification of the energy terms in the presentation of unrigid point and surface groups [22, 26]. But attempts were made to preserve the graphicalness of the analysis using geometrical ideas [23] and the theory of graphs [24, 25]. Of special interest is the dynamic charge in compounds with mixed valency. Several dimer compounds, $[X_kM - Y - MX_k]^{z\pm}$, have been obtained in coordination chemistry. The formal charge or the oxidation degree of metal atoms in these compounds must be different. These are compounds of two- and three-charge iron, cobalt, and ruthenium; three- and five-charge tungsten, and so on. The charge on the metal atoms in the dimers corresponds to such an occupation of molecular orbitals at which one- or two-electron transfer between metal atoms can be realized.

Consider a ruthenium dimer as an example:



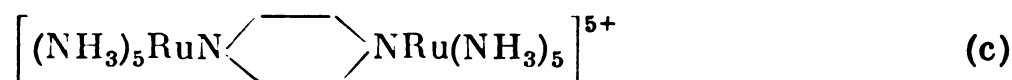
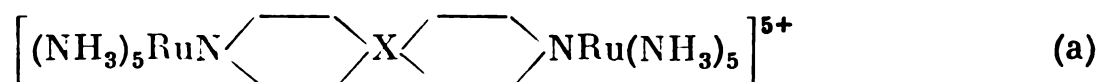
These ruthenium atoms are mixed-valent, RuII-RuIII. The molecular orbitals $RuN \langle \text{pyrazine} \rangle NRu$ can be written in the form of a linear combination of the lowermost π^* -orbitals of pyrazine with $4d$ -orbitals of Ru. Three molecular orbitals are thus important: the bonding orbital ψ_{bond} , mainly of the metal atoms; non-bonding orbital of the metal atoms $\psi_{\text{non-bond}}$; and the antibonding orbital ψ_{antibond} which is mainly the antibonding orbital of ligands [27].

In the five-charge dimer, two electrons are located in the ψ_{bond} and one electron in the non-bonding orbital of a metal. The velocity of the electron exchange between the metal atoms depends on the degree of screening of the electron movement by the bridge atom group and on the overlapping of the metal atom valency orbitals. If the overlapping is significant and the barrier for the electron transfer is absent the average charge corresponding to the electron delocalization will be observed. If the interatomic action between metal atoms is weak, the electron movement can be considered to occur in the field characterized by the presence of a potential barrier. The tunnel-activating mechanism is probably realized in dimers, when the activation component is added to the tunnel process. So, in a certain length of time τ , the charge on the metal atom changes from q to n :



If the characteristic time $\Delta t \gg \tau$, then the electron will change its position several times during the observation period and the average charge will be observed on the metal atom (in the volume of the metal atom). If however $\Delta t \ll \tau$, the electron position will alternately be detected instrumentally in either of the potential wells with fixation of the non-stationary charge.

The dependence of the electron life time on the nature of a bridge ligand has been studied in many works where dimers of ruthenium were used as examples [9, 27]*:

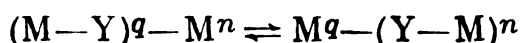


The electron exchange in (a) occurs in the lapse of 10^{-2} sec for $\text{X} = \text{Si}$ and CH_2 . It is much faster (10^{-13} sec) in (d), because the CN groups do not produce any barrier to the electron exchange. The photo-emission spectra show that the electron exchange in (c) occurs during 10^{-15} sec. As to the type (b) cation, various authors [9] are unanimous in their opinion that there is a weak interaction between metal atoms, and non-stationary valency of ruthenium can therefore be observed.

In the considered examples, the bridge ligand is a sufficiently rigid structure, and as the electron moves, the ligand atoms are only insignificantly displaced from the equilibrium position. The sec-

* Here and further we shall refer to review articles [9, 27].

ond limit case corresponds to the situation when the electron is to a considerable degree localized in the bridge ligand. Such an electron will be involved in the process of changing of the charge on the metal atoms, provided it has two energetically equivalent positions along the line of the chemical bond and performs quantum-mechanical vibrations from one position into another



The monodimensional movement of a ligand carrying an electron can be described in the field of two symmetrical potential wells divided by a barrier. When the ligand is in either of the wells, the nearest metal atom is reduced while the other atom is oxidized. The simplest oxidation-reduction process takes place. The time of the ligand penetration through the barrier determines the life time of the unstationary metal atom charge. Of course, in real systems, the charge oscillation process is neither purely electronic nor purely phononic. This is a complicate electron-phonon process.

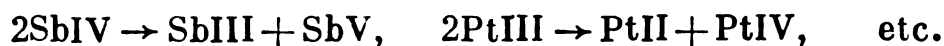
Using the concepts developed for the one-electron process, let us now consider the two-electron exchange. The dimer $K_4[Cl_5WOWCl_5]$ can be a good example, in which the atoms of tungsten have similar anion arrangement and different charge: WIII-WV [9, 27].

The wave function for two electrons in the field of similar metal ions can be described as this:

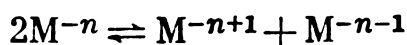
$$\Phi = C_1 \{ \varphi_{M_1(1)} \varphi_{M_2(2)} + \varphi_{M_1(2)} \varphi_{M_2(1)} \} + C_2 \{ \varphi_{M_1(1)} \varphi_{M_1(2)} + \varphi_{M_2(1)} \varphi_{M_2(2)} \}$$

where the parenthesized indices refer to electrons, and the indices at M enumerate the metal atoms. The first two terms correspond to a completely delocalized electron state and to the dissociation of the dimer into two equivalent ions, while the last two terms give the ionic component and the corresponding dissociation into two different ions, when both electrons are on either of the metal atoms.

There are many examples in chemistry of complex compounds where C_2 is large, i.e. the ionic term is great. In this case the disproportionation is energetically profitable and is accompanied by the localization of two electrons on one centre:



In accordance with the chemical concepts, the disproportionation reaction is energetically advantageous:



provided the free energy diminishes, i.e. $\Delta F < 0$. The value of ΔF is determined by the expression

$$\begin{aligned} \Delta F = I(M^{-n+1}) - I(M^{-n-1}) + 2F(M^{-n}) - F(M^{-n+1}) - \\ - F(M^{-n-1}) = \Delta I - \delta F \end{aligned}$$

where I is the ionization energy of ions M in the gas phase and F is the solvating energy. For most simple ions M , the reaction of disproportionation into two electrons does not, as a rule, occur in the gas phase. It occurs only in solution and is accomplished not at the expense of ΔI but at the expense of the gain in solvation (or hydration) energy. As to the solid crystal state, the role of the medium (the solvent for ions) is performed by the ligands. The surface-sphere particles can be disregarded for their small energy corrections ($\delta F' \rightarrow 0$). The ions $\text{Sb}^{\text{IV}}\text{Cl}_6^{2-}$ exist neither in solution nor in the solid state. The reaction



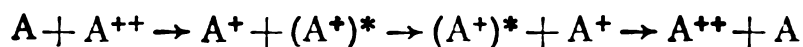
is shifted to one side and the following condition for the total energy is fulfilled:

$$2E_{\text{SbIV}} > E_{\text{SbV}} + E_{\text{SbIII}}$$

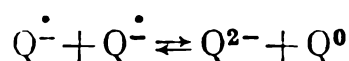
The magnitude δF includes only intramolecular forces, and then

$$\Delta F = \Delta I' = I(\text{SbCl}_6^2-) - I(\text{SbCl}_6^{3-}) < 0$$

Such relationships between the total energy and the ionization potentials indicate the effective attraction of the electrons on the centre SbCl_6^{3-} (as compared with SbCl_6^-). This description was first used in works [28-32]. It should be noted, however, that ordinary Coulomb forces are responsible for the inter-electron action in the ion SbCl_6^{3-} and the effective attraction $\Delta I' < 0$ of electrons can only be discussed in relative sense. Regarding two electrons as one particle in the process of oscillation $\text{SbIII} \rightleftharpoons \text{SbV}$ leads us to the same conclusion about the time electron localization as in the case with one-electron transfer. The problem of the two-electron exchange is important in the gas phase too. It turned out that the probability of the two-electron exchange can be high in the reaction



Disproportionation can occur with the participation of anion radicals of organic molecules, e.g. quinones (Q):



Let us discuss now the effect of the electron density redistribution connected with the order in crystals. If dimers form one-dimensional chains or columns in the crystal lattice, and the interaction energy of electrons (or electron pairs) between dimers is higher than kT , a spontaneous electron polarization or cooperative electron ordering can arise in a crystal, when electrons are localized either in α or in β potential well. This is the stationary localization, at which metal atoms M^n and M^q , bearing different charges, live infinitely long lives. The difference in the electron densities on two neighbouring

centres is the ordering parameter $m = (q - n)/2$, and it can be expressed by any fractional number. "Rigid" dimers are the simplest systems in which dynamic "purely" electronic processes can be observed, which change valency. The cooperative effect adds specificity to the processes of electron localization; to be more exact, it orders the localization of electrons, which means orderly disproportionation of charges on the atom centres. The state characterized by the divided charge corresponds to the stationary localization of electrons and it can be realized at temperatures below a certain critical point.

Recent investigations [28-33, 36-38] convincingly show that the processes of orderly electron localization in organic and inorganic substances can be referred to the category of the fundamental and frequently occurring properties of the solid state. The study of the electron transformations at the junction of two phases, with the ordered and average charge, involves the solution of problems connected with the time dependence of charge, its dynamics, and collective excitations [29, 30, 38], etc.

First of all, consider what types of the electron-ordered states can arise in crystals. Let us illustrate this classification by a crystal built of identical atoms (centres); two orbitals take part in the formation of energy bands on each of them.

(1) If the ordered centres differ from one another only in electron densities*, the state is known as the charge-ordered state (COS).

(a) The charge-ordered state is sub-divided into two types. COS I, when ordering results from Coulomb repulsion of electrons. COS I is realized when the Coulomb interaction between electrons on the neighbouring centres $zV_{\alpha,\beta}$ is stronger than the repulsion of electrons on one centre I_α . The difference in these interactions determines the ordering parameter m , i.e. determines the charge on the atom centre in the lattice. As the environmental factors (temperature, pressure) change, COS I transforms into the state with averaged charge, and variable "valency" disappears in the transition into the metal phase.

(b) COS II is the state characterized by the order arising from effective electron attraction on the centre. In COS II, the intercentre Coulomb action determines the ordering parameter which can vanish long before the substance changes into a metal under the effect of the changing environmental factors.

(2) The so-called charge-orbital ordered state (COOS) can also arise. The atoms become different with respect to both electron density on the centre and orbitals on the centre. Orbitals of one type on different centres are characterized by different electron densities. COOS I is the state when both types of order are observed. COOS II

* The centres themselves are identical in composition and geometry.

is the state when electron ordering occurs only in orbitals, and the total electron density is the same on all centres.

(3) Orbital-order state (OOS). The electron density on centres and in orbitals is the same. Centres are differently oriented in space. For example, an elongated octahedron alternates the axial direction from centre to centre. Many examples of crystals with various ordering types can be given [33]. Ordering on the basis of the disproportionation reaction, when an effective attraction arises on the centre, is most interesting. Thus, crystals $K_2Sb\Gamma_6$ (where K is the cation and Γ is Cl, Br) have an insular* structure and are composed of octahedral complexes $Sb\Gamma_6^{n-}$ (where n is 1 or 3). X-ray diffraction methods show that both ordered (COS II) and disordered structures can be realized. The latter have face-centred cubic lattice. Disordered and ordered crystals are dielectrics and diamagnetics.

Theoretical calculations show [38] that COS is characterized by the existence of collective excitations inside a one-particle energy gap, which correspond to the charge transfer and cause low-temperature spreading of electron density. Proceeding from theory, one can give the following qualitative scheme of possible electron excitations for the ground state COS.

In COS I, inside the one-particle gap Δ , there is the only collective mode which corresponds to the bound electron state in the conductivity band and the valent band hole. In COS II, there are at least two collective branches with energies less than Δ , of which one corresponds to the two-electron density fluctuations on the centres. The unique characteristics of the structure of the excited state levels in COS II give us the hope that the paired electron current, and probably also high-temperature superconductivity may be discovered and studied.

There is another type of compounds, such as SmS, which turn into mixed-valent ones under high pressures. But only static charge is always observed on them [39-41]. Under normal conditions, SmS

Excitation character	Excitation energy
1. Unpairing of electron on an arbitrary vacant centre	$4V_{\mu\nu} - I_\nu$
2. Unpairing of electron on the neighbouring centre	$3V_{\mu\nu} - I_\nu, \quad (T = 0)$ $2V_{\mu\nu} - I_\nu, \quad (T \neq 0)$
3. Electron pair transfer on an arbitrary vacant centre	$8V_{\mu\nu}$
4. Electron pair transfer on the neighbouring centre	$4V_{\mu\nu}$

* An insular structure is that consisting of isolated complexes without bridge ligands.

has the structure of rock salt and is an ionic semi-conductor, while under a pressure of 6 Kbar it has a metal-type conductivity and an averaged (between SmII and SmIII) charge. The cooperative division of the charge due to cooperative localization of electrons does not take place in such compounds.

Dynamics, effective charge, valency. The ability of an atomic or a molecular centre to add atoms or atom groups, and also geometry (stereochemistry) and the coordination number, from the standpoint of modern theoretical chemistry is determined by the minimum energy, i.e. profitability of the state.

The discovery of unrigid molecular systems both in gas and in condensed phases drew investigators' attention to the elementary molecular dynamics, where a system can have two or several similar or only insignificantly differing energy minima. As a matter of fact, these processes (both electron-vibratory and electronic) are the simplest chemical reactions. In this aspect, the idea of changing coordination number or the distortion degree and the change of the charge with time can be included into the valency concept provided the latter term means the ability of atomic or intermolecular centres to show certain tendencies during formation of chemical bonds both in dynamic and in static sense.

The valency of an atom, i.e. its ability to form chemical bonds, is one of the fundamental concepts in chemistry. It is difficult to name another branch of the theory of molecular structure which developed as vigorously as the theory of valency. It has passed a long way from the primitive electrostatic concepts, through the theory of localized bonds by Heitler-London and Bethe-van Vleck theory of crystal field to the modern theory of molecular orbitals based on the idea of Mulliken, Hartree, and Fock. Numerous modifications of the molecular orbital method are a combination of methods of approximated solution of the Schrödinger equation, mainly for stationary many-electron systems. These solutions give stationary eigenvalues and eigenfunctions, and hence stationary, the only, distribution of electron density which corresponds to the stationary valency. The molecular orbital method, being a commonly adopted theory of structure of inorganic compounds, has significantly advanced our understanding of stationary distribution of electron density in molecules, of the nature of the chemical bond in such compounds to which the concepts of two-electron, two-centre chemical bonds are inapplicable. Of course, this *old* problem of the nature of the chemical bond will always remain *modern* for compounds comprising atoms with complex electron shells and requiring consideration of such intimate effects as the relativity and correlation ones.

At the same time, the highly precise structural and radiospectroscopic methods make it possible to pass over to qualitatively new solution of the valency problem connected with its dynamic aspect.

The problems connected with possible electron transfer in systems with a two-well potential are now studied on the basis of the EPR-spectra of organic anions such as dibenzyl, stilbene, azobenzene, etc. The quantum-mechanical interpretation of these data makes it possible to develop some general postulates of the theory of redistribution of electron density on atomic centres, time and stationary localization of electrons. All these processes are substantially intensified in the crystal lattice by the cooperative effect and can give leap-form changes in valency of all lattice points.

The problem of correlation of the cooperative processes and valency is connected with the problems of major importance associated with the time dependence of electron re-grouping. This problem cannot be solved by the methods giving stationary solutions. But this is very important for chemistry, because in chemical processes it is hardly possible to limit oneself to the stationary states, which do not bear any information on the electron dynamics. This, first of all, refers to the study of catalytic activity and rates of chemical reactions involving one or several centres of a large molecule and depending on the electron density at the site of attack. And finally, there are compounds which contain heterovalent ions of one and the same element, whose properties cannot in general be interpreted in the terms of the concepts of stationary states and stationary (fixed) valency. These are known as compounds with "fractional valency", "mixed oxidation", "oscillating valency", "fluctuating valency". Although none of these names fully describes the essence of the problem, they show the attempt to describe the dynamic effect. These compounds have a long history; they were studied by Berzelius and Werner. It has now been established that at least forty elements of the Periodic system can form such compounds. As a rule, they are characterized by unique properties and have many practical uses. Their specific properties are mainly due to the dynamic re-arrangement of electrons which depends on time and conditions (temperature and pressure).

The problems of dynamics, the problem of charge, geometry, and time correspondence are especially important in biological systems, where various processes are intimately interconnected at different levels: electronic, phononic, electron-vibratory, excitonic, and so on. We think that it is biology and biophysics that will widen our knowledge of the properties of atoms and molecules and deepen the concept of "dynamic valency".

References

1. Hund, F., *Physik*, 43, 805, 1927.
2. Oppenheimer, J. R., *Phys. Rev.*, 13, 66, 1928.
3. Nordheim, L., *Z. Physik*, 46, 833, 1927.
4. Gamov, G., *Physik*, 51, 204, 1928.

5. Jahn, H. A., Teller, E., *Proc. Roy. Soc.*, **161**, 220-267, 1937.
6. Bersuker, I. B., *Electron Structure and Properties of Coordination Compounds*, Khimia, Leningrad, 1976, p. 192-241 (in Russian).
7. Voevodsky, V. V., Blumenfeld, L. A., *Zh. vsesoyuzn. khim. obshch. im. Mendeleeva*, **7**, 457, 1962 (in Russian).
8. Blumenfeld, L. A., Goldansky, V. I., Podgoretsky, M. I., Chernavsky, D. S., *J. Struct. chem.*, **8**, No. 5, 854, 1967.
9. Ionova, G. V., *Zh. fiz. khim.*, **52**, 6, 1374-1387, 1978 (in Russian).
10. Chernavskaya, N. M., Chernavsky, D. S., *Tunnel Transport of Electrons and Photosynthesis*, Moscow University Press, 1977 (in Russian).
11. Longuet-Higgins, H. C., *Mol. Phys.*, **6**, 445, 1963.
12. Altmann, S. L., *Proc. Roy. Soc.*, **A298**, 184, 1453, 1967.
13. Dalton, B. I., *Mol. Phys.*, **11**, 3, 265, 1966.
14. Woodman, C. M., *Mol. Phys.*, **19**, 6, 753, 1970.
15. Ovchinnikov, Y. N., Ionov, S. P., *ZhETP*, **53**, 8, 598, 1967 (in Russian). Spiridonov, V. P., Ishchenko, A. A., Zasorin, E. Z., *Usp. khimii*, **47**, 1, 101, 1978 (in Russian).
16. Seward, W. D., Narayanamurti, V., *Phys. Rev.*, **148**, 463, 1966.
17. Prokofiev, A. I., Malysheva, N. A., Bubnov, N. N., Solodovnikov, S. P., Belostotskaya, I. S., Komissarova, N. L., Ershov, V. V., Kabanchik, M. I., *DAN SSSR*, **229**, 1396, 1128, 1976 (in Russian).
18. Sokolov, N. D., *Zh. vses. khim. obshch. im. Mendeleeva*, **17**, 3, 299, 1972 (in Russian).
19. Ionov, S. P., Ionova, G. V., *Zh. fiz. khim.*, **46**, 4, 845, 1972 (in Russian).
20. Ionov, S. P., Ionova, G. V., *Izv. AN SSSR, ser. chem.*, **12**, 2836, 1970 (in Russian).
21. Ionov, S. P., Ionova, G. V., Porai-Koshits, *DAN SSSR*, **193**, 1, 129, 1970 (in Russian).
22. Kotakowski, B., *Acta Physica Polonica*, **A52**, 5, 635, 1977.
23. Muettert, E. L., *JACS*, **91**, 7, 1636, 1969.
24. Gialen, M., Depasse-Delit, C., *Teoret. Chem. Acta*, **14**, 3, 212, 1969.
25. Heller, I., *Chimia*, **23**, 10, 351, 1969.
26. Holmes, R. R., Deiters, R. M., Golden, J. A., *Inorg. Chem.*, **8**, 12, 2612, 1969.
27. Ionova, G. V., Ionov, S. P., Makarov, E. F., *Zh. fiz. khim.*, 3736-76, p. 1-23, 1976 (in Russian).
28. Ionov, S. P., Ionova, G. V., Lubimov, V. S., Makarov, E. F., *Phys. stat. sol.*, (b), **71**, 11-57, 1975.
29. Ionov, S. P., Lubimov, V. S., Makarov, E. F., Ionova, G. V., Uimin, G. V., *Phys. stat. sol.*, (b), **72**, 515, 1975.
30. Lubimov, V. S., Ionova, G. V., Pachev, O. M., Manakova, L. A., Makarov, E. F., Ionov, S. P., *Phys. stat. sol.*, **75**, 91, 1976.
31. Ionova, G. V., Makarov, E. F., Ionov, S. P., *Phys. stat. sol.*, (b), **81**, 671, 1977.
32. Manakova, L. A., Makarov, E. F., Ionov, S. P., *Phys. stat. sol.* (b) **84**, 55, 1977.
33. Ionova, G. V., Makarov, E. F., Pachev, O. M., Ionov, S. P., *Phys. stat. sol.* (b), **85**, 683, 1973.
34. Chibisov, M. I., *ZETF*, **4**, (10), 75, 1978 (in Russian).
35. Khudyakov, I. V., Kuzmin, V. A., *Usp. khimii*, **47**, 1, 60-61, 73, 1978 (in Russian).
36. Ionova, G. V., Ionov, S. P., *Izv. AN SSSR, ser. fiz.*, **42**, 6, 1296-1315, 1978 (in Russian).

37. Goldansky, V. I., *Vestnik AN SSSR*, 3, 36, 1976 (in Russian).
38. Lyubimov, V. S., Manakova, L. A., Ionov, S. P.,[†] Semin, G. K., *Izv. AN SSSR, ser. fiz.*, 42, 6, 1316-1340, 1978 (in Russian).
39. Varma, C. M., *Rev. Mod. Phys.*, 48, 2,[†] 219, 1976.
40. *Valence Instabilities and Related Narrow-band Phenomena*, Ed. R. D. Parks, New-York, London, Plenum Press, 1977.
41. Menezes, O. L. T., Troper, A., Lederer, P., Gomes, A. A., *Phys. Rev. B* 17, 4, 1977 (1978).

Comparative Assessment of the Main Quantum- chemical Methods

The quantum-chemical interpretation of valency by the valence-bond and molecular-orbital methods was discussed in Chapters 5 and 7. In this chapter we shall slightly depart from the historical succession and will consider, in more detail, the correlation of these methods. It will help us better understand quantum chemistry of molecules, the branch of chemistry which was formed in the past fifty years. This, in turn, will give us definite criteria by which we can assess the quantum-chemical theories of valency.

1. Main Quantum-chemical Approximations

Quantum chemistry is a result of extension of the quantum mechanical methods to all fields of chemistry. Quantum chemistry of molecules is of special interest in the context of this book.

It should be noted that there is no sharp boundary line between the objects of study in various branches of theoretical physics and quantum chemistry. For example, the objects of chemical studies are not only molecules but also defects in crystals, unstable aggregations which appear in the course of chemical reactions, molecular complexes in various solutions, etc. All these systems are called *molecules* in quantum chemistry.

The specificity of objects differentiates quantum chemistry from other sciences, for example, from the theory of atomic collisions, or physics of the solid state. Quantum chemistry does not contain any new physical ideas compared with the postulates of quantum mechanics. But the specific character of chemical objects stimulated the creation of special methods by which the Schrödinger equation can be given approximate solutions. Quantum chemistry has developed its own language, terminology (molecular orbitals, hybridization, conjugation energy, etc.). This language, to a considerable extent conventional, gives a loose, and in some cases only indirect information on the structure and properties of molecules, and the course of chemical processes. Nevertheless the language is very useful and can often not only explain but also predict the physico-chemical

properties of molecules. And what is important here, is correct understanding of what is meant by this or that quantum-chemical term, the limits within which these terms can be used, and actual physical values with which they can be correlated. In other words, it is necessary to remember the principles of quantum mechanics when using quantum-chemical terminology.

We shall not describe these principles here, but only remind some points which are closely related to quantum chemistry.

1. As a rule, quantum chemistry deals with a model of infinitely long living microsystems. In other words, the potential energy of a microsystem is considered to be independent of time (stationary case). The time factor $e^{-i\mathcal{E}t}$ can therefore be separated and only the coordinate part of the wave function can be found by solving the stationary Schrödinger equation:

$$\hat{\mathcal{H}}\Psi = \mathcal{E}\Psi \quad (9.1)$$

where $\hat{\mathcal{H}}$ is the Hamiltonian of the system and \mathcal{E} is the full energy of the system.

2. These are not all solutions of the equation (9.1) which suit the purpose but only those for which $\mathcal{E} < 0$ (discrete spectrum). The corresponding wave functions Ψ describe stable states of the microsystem. In this case the function $|\Psi|^2$ can be ascribed the sense of density of probable presence of particles at certain points of the coordinate-spin space. The character of the wave function (exponential diminishing to infinity) indicates a certain localization of electrons and nuclei in space, i.e. it is possible to define a molecule as a chemical object having definite dimensions.

3. Molecules consist of nuclei and electrons. Since the mass of the electron is considerably less than the mass of any nucleus (the ratio of the electron mass to the mass of the lightest nucleus, proton, is 5.44×10^{-4}), the adiabatic approximation* is used in many quantum-chemical problems. Its essence is as following. Let \vec{R} and \vec{r} be sets of coordinates of nuclei and electrons respectively. Let us find the approximate wave function of the system in the form of a product of the electron wave function $\psi(\vec{r}; \vec{R})$ and the nuclear wave function $f(\vec{R})$. The function $\psi(\vec{r}; \vec{R})$ describes the motion of electrons with fixed nuclei (i.e. at a given nuclear configuration) and is the solution of the adiabatic Schrödinger equation:

$$\hat{H}\psi(\vec{r}; \vec{R}) = E(\vec{R})\psi(\vec{r}; \vec{R}) \quad (9.2)$$

* This approximation does not hold for so-called meso-molecules.

The operator \hat{H} of the electron motion differs from $\hat{\mathcal{H}}$ in that it does not contain any kinetic energy operator of nuclei $T_{\vec{R}}$ (the nuclei are assumed to be stationary), i.e.

$$\hat{\mathcal{H}} = \hat{H} + \hat{T}_{\vec{R}} \quad (9.3)$$

If external electrical or magnetic fields are not introduced, and the spin-orbital interactions of the electrons and the relativity effects are disregarded, then the operator \hat{H} of the system of N electrons in the nuclei field can be represented as follows:

$$\hat{H} = \sum_{\mu=1}^N \hat{h}(\mu) + \frac{1}{2} \sum_{\mu, \nu}^N \frac{1}{r_{\mu, \nu}} + \frac{1}{2} \sum_{u, v} \frac{Z_u Z_v}{R_{uv}} \quad (9.4)$$

where

$$\hat{h}(\mu) = \hat{t}(\mu) - \sum_{u=1}^N \frac{Z_u}{r_{u\mu}} \quad (9.5)$$

$\hat{h}(\mu)$ is the one-electron operator of kinetic energy (\hat{t}) of the μ th electron and of the potential energy of the μ th electron interaction with the nuclei; u, v are subscripts designating the nuclei; Z_u is the charge on the u th nucleus; the second term in (9.4) is the energy operator of the electron interaction energy; the third term of (9.4) is the nuclear interaction energy; R_{uv} is the distance between the u th and v th nuclei.

The function $\psi(\vec{r}; \vec{R})$ and the energy $E(\vec{R})$ depend on the nucleus coordinates as parameters. Solving the equation (9.2) we obtain a set of potential surfaces $E_i(\vec{R})$ and the corresponding electron wave functions $\psi_i(\vec{r}; \vec{R})$. The configuration of nuclei \vec{R}^0 , corresponding to the energy minimum*, determines the stable formation, a molecule with equilibrated values of bond lengths and valency angles. It is evident that each i th electron state is characterized by its equilibrium configuration of nuclei.

The other aspect of the adiabatic approximation is the calculation of the functions $f_i(\vec{R})$ characterizing the motion of nuclei in the i th electron potential $E_i(\vec{R})$. This problem has a straight way into the theory of molecular oscillations, the conformational analysis, and kinetics of elementary reactions. The set of functions $f_{im}(\vec{R})$ and energy levels \mathcal{E}_{im} for each i th electron state can be obtained from the following equation:

$$[\hat{T}_R + \mathcal{E}_i(\vec{R})] f_{im}(\vec{R}) = \mathcal{E}_{im} f_{im}(\vec{R}) \quad (9.6)$$

* To be more exact, there are several such minima.

But we can often assume that heavy particles, i.e. nuclei, move along classical trajectories, and the corresponding classical problem can be solved instead of (9.6). The adiabatic approximation can be used only if the energy surfaces, corresponding to various electron states, are separated from each other to a considerable distance*. As a rule this holds for equilibrium configuration \vec{R}^0 of the ground electron state ($i = 0$).

4. Many quantum-chemical problems can be solved by considering purely electron states, i.e. by solving the equation (9.2) for the ground and several lower excited states. The equation (9.2) is usually solved by the variation principle.** To understand it, let us multiply both parts of the equation (9.2) on the left by ψ^* and integrate by all electron variables (i.e. all spatial coordinates of \vec{r} and spin variables σ). The function of the discrete spectrum is usually normalized to unity

$$\int |\psi(\vec{r}; \vec{R})|^2 dv d\sigma = 1 \quad (9.7)***$$

Therefore

$$E(\vec{R}) = \int \psi^* \hat{H} \psi dv d\sigma \quad (9.8)$$

The equation (9.8) is valid for accurate solution of the equation (9.2). If now, in the integral standing in the right-hand part of the equation (9.8), we substitute any approximate function $\tilde{\psi}$, fulfilling the condition

$$\int |\tilde{\psi}|^2 dv d\sigma = 1 \quad (9.9)$$

for the accurate solution of the equation (9.2), we have

$$J(\vec{R}; \tilde{\psi}) = \int \tilde{\psi}^* \hat{H} \tilde{\psi} dv d\sigma \quad (9.10)$$

the integral, whose value for each configuration of \vec{R} depends on the type of function $\tilde{\psi}$. If no additional conditions are imposed on $\tilde{\psi}$ (except those specified in 9.9), we have the following:

$$I(\vec{R}; \tilde{\psi}) \geq E_0(\vec{R}) \quad (9.11)$$

where $E_0(\vec{R})$ is the energy surface of the ground electronic state.****

* For details see Ref. [2].

** The variation method is not the only method to solve the equation (9.2). The so-called metal model is another possible approach.

*** This equality must be fulfilled with any set of nuclear coordinates for \vec{R} .

**** The proof of the inequality (9.11) can be found, e.g. in the book by Tatevskii [3].

As a rule, a whole class of test functions $\tilde{\psi}$, depending on the parameters, are considered, and the functional minimum (9.10) is sought for in the given class of functions. It is evident that the function $\tilde{\psi}$ ensuring this functional minimum gives the best approximation of $I(\vec{R}\tilde{\psi})$ to $E_0(\vec{R})$ in the given class of functions and is, on an average, the nearest among all other functions of the given class, to the exact solution of the equation (9.2).

5. While limiting ourselves to solving only electronic problems (i.e. solving the equation 9.2) we consider the molecule as a many-electron system in the potential field of point charges (see the evident type of operator \hat{H}). The wave function of such a system can be characterized by the symmetry of its spin component. In other words, it is necessary that the function ψ be the eigenfunction of the full spin square operator of the system of N electrons (\hat{S}^2) and operator of the full spin projection on a certain direction (\hat{S}_z), i.e.

$$\hat{S}^2\psi = S(S+1)\psi \quad (9.12)$$

$$\hat{S}_z\psi = M_S\psi \quad (9.13)$$

where S and M_S are full spins of the system of N electrons and their projection onto the axis z .

The conditions of (9.12) and (9.13) are usually superimposed onto the function ψ before the equation (9.2) is solved.* Thus the class of the sought functions ψ can be verified beforehand.

The conditions 1-5 considered above are rather typical of quantum-chemical problems, though in various combinations, these conditions are used to solve other problems in theoretical physics as well. As far as the quantum-chemical methods proper are concerned, they give only tentative solutions of the equation (9.2).

We shall discuss only two quantum-chemical methods, *viz.*, the molecular-orbital (LCAO) and the valence-bond method. First of all, they can be used to calculate the electron structure for a sufficiently large number of chemical objects, and secondly they are studied well enough not only in the theoretical but in practical aspect as well. And what is more important, these two methods can answer the question what the valency of an atom is, and give the mathematical definition of this concept.

The molecular-orbital and valence-bond methods appeared almost simultaneously at the end of the 1920s. There were two trends in their application: (1) non-empirical calculation of simplest mole-

* An example of another approach to the theory of many-electron systems is the unrestricted Hartree-Fock method (see, e.g., the book by McWeeny and Sutcliffe, [4]).

cules; (2) development of semi-empirical variants of both methods, and qualitative solution of various physico-chemical problems

Till the early 1950s, i.e. before the first generation of the fast-acting computers was developed, semi-empirical methods and qualitative conceptions of quantum chemistry had predominantly been developing. The advances in the computing technique have resulted not only in accumulation of quantitative characteristics of molecules but promoted the creation of new qualitative conceptions. In some cases the old concepts were revised and deepened. It is necessary to note that the formulation of the molecular orbital theory of valency, which was given in Chapter 7, would have been of little practical value before the creation of fast-acting computers and calculation methods, because its application to the study of the valency structure of chemical compounds, which extended beyond the scope of the classical theory of valency, would have been impossible.

The first of the two trends (i.e. non-empirical methods) is of interest only for specialists working in the field of quantum chemistry. But the latter was very soon appreciated and widely used by chemists of all specialities, because it gave simple and comprehensive explanations to a wide range of chemical problems. One should not necessarily be acquainted with quantum mechanics. It is enough only to know certain uncomplicated techniques which proceed logically from simplified variants of the molecular-orbital (LCAO) and valence-bond methods. This simple semi-empirical scheme based on the VB method was used in the attempts to explain the formation of molecules from atoms, directionality of bonds, and geometry of molecules. It should be remembered, however, that such "explanations" (which are actually only illustrative descriptions) often have a very shaky foundation. The effectiveness of the MO and VB methods is directly related to the problem of atom valency and we shall therefore discuss and compare them in more detail.

2. Mathematical Principles of the MO and VB Methods. Non-empirical Calculations

MO (LCAO) Method. The molecular orbital method is also known in the theory of many-electron systems as the one-electron approximation. Its essence is the determination of approximate characteristics of each separate electron, i.e. the description of motion of each electron of the system in the field of nuclei and an effective field of other electrons. This approach makes it possible to solve the equation (9.2) for a many-electron wave function as the equation for a one-electron system.

The many-electron function ψ_{MO} , approximating the exact solution of the equation (9.3) for the ground state of a system with a

closed shell, is modified in the MO method into the following:

$$\psi_{\text{MO}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(1)\beta(1) & \dots & \varphi_{\frac{N}{2}}(1)\beta(1) \\ \varphi_1(2)\alpha(2) & \varphi_1(2)\beta(2) & \dots & \varphi_{\frac{N}{2}}(2)\beta(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(N)\alpha(N) & \varphi_1(N)\beta(N) & \dots & \varphi_{\frac{N}{2}}(N)\beta(N) \end{vmatrix} \quad (9.14)$$

Here $\psi_p(\vec{r})$ is the one-electron function of space coordinates (molecular orbital); $\alpha(\sigma)$ and $\beta(\sigma)$ are one-electron spin functions; \vec{r}_μ and σ_μ are arguments for each μ th electron (the corresponding electron numbers are used in the formula).

For convenience of further calculations we must simplify the function constructed in the form of the Slater determinant; the N -electron function thus modified, and characterized by similar numbers of $N/2$ functions $\alpha(\sigma)$ and $\beta(\sigma)$ but having, generally speaking, different coordinate functions $\varphi_1(\vec{r}) \dots \varphi_N(\vec{r})$, will be written thus:

$$\psi = [\varphi_1 \overline{\varphi}_2 \varphi_3 \overline{\varphi}_4 \dots \varphi_{N-1} \overline{\varphi}_N] \quad (9.15)$$

Here we have only coordinate functions characterizing the determinant columns; the absence of a dash means multiplication by $\alpha(\sigma)$, and the dash indicates multiplication by $\beta(\sigma)$. It is important that the columns α and β alternate in our notations. The function (9.14) has the following form:

$$\psi_{\text{MO}} = [\varphi_1 \overline{\varphi}_1 \varphi_2 \overline{\varphi}_2 \dots \varphi_{\frac{N}{2}} \overline{\varphi}_{\frac{N}{2}}] \quad (9.16)$$

Conditions of ortho-normalization are usually imposed on the molecular orbitals ψ_p which are components of (9.14):

$$\int \psi_p^*(\vec{r}) \psi_q(\vec{r}) dv = S_{pq} \quad (9.17)$$

In this case the function (9.14) automatically meets the conditions of (9.7). Molecular orbitals are given in a certain class of functions meeting the requirements of (9.17) and can be determined from the conditions of the functional minimum:

$$J_{\text{MO}}(\vec{R}; \tilde{\psi}_{\text{MO}}) = \int \tilde{\psi}_{\text{MO}}^* \hat{H} \tilde{\psi}_{\text{MO}} dv d\sigma \quad (9.18)$$

The function $\tilde{\psi}_{\text{MO}}$ has the form of (9.14) with variation of all $N/2$ MO $\tilde{\psi}_p(\vec{r})$. Depending on the class of test functions $\tilde{\psi}_p$ several variants of the MO method can be distinguished. The most exact of them is the Hartree-Fock method in which the optimized one-electron func-

tions ψ_p , ensuring the functional minimum (9.18), are sought for. In Roothaan's method, the molecular orbitals are given in a narrower class of functions having the form of linear combinations of the finite number of certain basis functions $\chi_1(\vec{r}) \dots \chi_m(\vec{r})$:

$$\tilde{\varphi}_p = \sum_{k=1}^m \tilde{C}_{kp} \chi_k(\vec{r}) \quad (9.19)$$

where \tilde{C}_{kp} are variable parameters.

The number of basis functions depends on the number of electrons in the system:

$$m \geq \frac{N}{2} \quad (9.20)$$

The sign of equality corresponds to the minimum basis set.

Substituting the formulas (9.14) and (9.19) in (9.18), and taking into consideration (9.17), we obtain the expression for the energy functional:

$$\begin{aligned} J_{\text{MO}}(\vec{R}; \tilde{\psi}_{\text{MO}}) &\equiv \tilde{E}_{\text{MO}} = \\ &= \sum_{k,l=1}^m \tilde{P}_{lk} \left[h_{kl} + \frac{1}{2} \sum_{s,t=1}^m \tilde{P}_{ts} \left(\langle lk | ts \rangle - \frac{1}{2} \langle tk | ls \rangle \right) \right] \end{aligned} \quad (9.21)$$

Here

$$\tilde{P}_{lk} = 2 \sum_{p=1}^{\frac{N}{2}} \tilde{C}_{lp} \tilde{C}_{kp}^* \quad (9.22)$$

are the elements of the electron density matrix;

$$h_{kl} = \int \chi_k^* \hat{h} \chi_l dv$$

are the so-called one-electron integrals;

$$\langle lk | ts \rangle = \int \frac{\chi_l(\mu) \chi_k^*(\mu) \chi_t(\nu) \chi_s^*(\nu)}{r} dv_\mu dv_\nu$$

are two-electron integrals.

The integrals h_{kl} and $\langle lk | ts \rangle$ with the fixed position of nuclei are determined only by the given basis χ_k ; the coefficients C_{kp} are found from the minimum conditions (9.18) and equations

$$\sum_{k,l=1}^m C_{kp}^* C_{lp} S_{kl} = 1 \quad (9.23)$$

where $S_{kl} = \int \chi_k^* \chi_l dv$ is the integral of the basis functions overlap. Equations (9.23) arise from (9.17) and are necessary for the determination of the sought coefficients*.

Before the 1950s, when the calculations were performed manually, and the systems with small numbers of electrons were considered, the minimum of the equation (9.18) was often determined by directly calculating the energy (9.21) by the given lattice of parameters C_{kp} **.

In 1951 Roothaan derived a system of equations for the determination of C_{kp} :

$$\sum_{l=1}^m [F_{kl} - S_{kl}\varepsilon_p] C_{lp} = 0 \quad (k = 1, 2, \dots, m) \quad (9.24)$$

Here

$$F_{kl} = h_{kl} + \sum_{s, t=1}^m P_{ts} \left[\langle lk | ts \rangle - \frac{1}{2} \langle tk | ls \rangle \right] \quad (9.25)$$

are the elements of the Fock matrix.

The latter depend on the sought coefficients C_{kp} , which makes the system of equations (9.24) non-linear. Solving this system together with the equation (9.23) we obtain a set of coefficients at χ_k and the one-electron energy ε_p for each one-electron state p . This energy is usually compared with the vertical potential of ionization (Koopmans' theorem). The system of Roothaan's equations is the analogue to the Hartree-Fock equations for one-electron functions given in the form of a linear combination of certain basis functions.

Solving the system of equations (9.24) and (9.23) we have, generally speaking, a greater number of molecular orbitals than we need [see the condition (9.20)], from which we have to select $N/2$ molecular orbitals which can give the least value of the full energy. Such molecular orbitals are, as a rule, selected by the criterion of the minimum values of ε_p , which cannot always ensure the minimum of full energy. In fact, using the equations (9.24), (9.23) we can rearrange the expression (9.21) for energy as follows:

$$E_{MO} = 2 \sum_{p=1}^{\frac{N}{2}} \varepsilon_p - \frac{1}{2} \sum_{k, l, s, t}^m P_{lk} P_{ts} \left(\langle lk | ts \rangle - \frac{1}{2} \langle tk | ls \rangle \right) \quad (9.26)$$

* There are methods for direct determination of the elements of the matrix P without preliminary determination of the coefficients C_{kp} (see, for example, Ref. [4]).

** This approach has become a foundation for McWeeny's method; see Ref. [4].

The first member in this expression is the sum of one-electron energies, i.e. the energies of each electron in the field of nuclei and self-consistent field of other electrons; the second term in (9.26) is the result of the electron interaction. Its value is of the same order as that of the energy of interaction of electrons with nuclei, and it is therefore impossible to disregard the second term in the equation (9.26).

Roothaan's method gives no hints as to the concrete form of the basis functions, nor does it give any additional approximations in the assessment of matrix elements. This method can be referred to the so-called *ab initio* methods in quantum chemistry. But for the correlation of the molecular-orbital and valence-bond methods, it is reasonable to arrive at a concrete basis, viz., the basis of atomic orbitals, i.e. one-electron functions centred at nuclei and which more or less well approximate the set of the Hartree-Fock functions for the corresponding atoms. Slater-type functions or sets of Gauss-type functions are commonly used as atomic orbitals. These mathematical details are not important for our future discussion.

The formalism of the LCAO method refers only to closed shell systems ($S = 0$, N is an even number). The function ψ_{MO} for open shell systems is more complicated than (9.14), and this makes the problem more difficult. It requires special discussion and we shall not consider it in this chapter.

The valence bond method. The wave function of a many-electron system can be written in the MO method in a sufficiently general and compact form. But in the valence bond method, the analytical expression of the function ψ can be obtained only for the hydrogen molecule. Therefore, in the general case of N electrons, it is reasonable to give the technique of constructing the wave function. First of all, both in the MO (LCAO) and VB methods, a molecule is mentally divided into atoms and the atomic basis χ_k is given. The next stage is the selection of electronic configuration.

Let us characterize each atomic orbital χ_k by the number of its electrons, i.e. by the occupation number. These occupation numbers of atomic orbitals in the VB method (like the occupation numbers of molecular orbitals in the MO method) can only be equal to zero, unity, and two. When we set the atomic orbitals and the corresponding occupation numbers, we give a certain electron configuration to each atom. For a further discussion we must define some terms.

Atomic orbitals (AO) containing one electron are known as valence orbitals; doubly-occupied AO's are orbitals of inner atom shells and of unshared pairs*.

* Sometimes, the concept of valence orbitals and valency electrons is extended to all orbitals with unoccupied atom shells.

The number of valence atomic orbitals (which is equal to the number of electrons in an atom with non-compensated spins) is known as *spin-valency* of an atom. This number is $2S$ (where S is the full spin of the atom).

Pre-giving the electron configuration to a molecule in the VB method is determined by the pre-set electron configuration of separate atoms. The selection is not simple, because the atom state can be characterized by a set of electron configurations. Giving only one configuration to a molecule, we proceed from the fact that, for each of its atoms, we can choose a configuration that will make it possible to build the optimum wave function for the molecule. We shall discuss this problem in more detail in the next paragraph, while here we shall only dwell on the mathematical formalism of the VB method.

Let the electronic configuration of a molecule containing N electrons have the form

$$\chi_1 \chi_2 \cdots \chi_n \chi_{n+1}^2 \cdots \chi_{n+l}^2 \quad (9.27)$$

where $2l + n = N$; $\chi_1 \cdots \chi_n$ are valence AO's; $\chi_{n+1} \cdots \chi_{n+l}$ are orbitals of inner and unshared pairs.

The wave function ψ_{VB} can be constructed as this:

$$\psi_{VB} = \sum_{k=1}^M C_k \Phi_k \quad (9.28)$$

where Φ_k is the Slater determinant [i.e. the function of the type (9.15)] for the configuration (9.27).

For example, the following Slater determinant can be constructed for the singlet-state function*:

$$\begin{aligned} \Phi_1 &= [\bar{\chi}_1 \bar{\chi}_2 \bar{\chi}_3 \bar{\chi}_4 \cdots \chi_{n-1} \bar{\chi}_n \chi_{n+1} \bar{\chi}_{n+1} \cdots \bar{\chi}_{n+l}] \\ \Phi_2 &= [\bar{\chi}_2 \bar{\chi}_1 \bar{\chi}_3 \bar{\chi}_4 \cdots \chi_{n-1} \bar{\chi}_n \chi_{n+1} \bar{\chi}_{n+1} \cdots \bar{\chi}_{n+l}] \\ \Phi_3 &= [\bar{\chi}_1 \bar{\chi}_2 \bar{\chi}_4 \bar{\chi}_3 \cdots \chi_{n-1} \bar{\chi}_n \chi_{n+1} \bar{\chi}_{n+1} \cdots \bar{\chi}_{n+l}] \\ &\dots \dots \dots \end{aligned} \quad (9.29)$$

etc., $M = n! / [(n/2)!]^2$ determinants altogether

The quantity M increases quickly with the growing number of valency electrons (e.g. for $n = 12$, $M = 924$), which makes the direct construction of ψ_{VB} from the formula (9.28) practically inapplicable to calculations. This difficulty can be removed by the transition to the so-called valency schemes (i.e. schemes of binding valency electrons).

* For the sake of convenience, we shall consider closed-shell systems ($S=0$, N an even number). Extension of the VB method to the systems with arbitrary N and S is discussed in the book by McWeeny and Sutcliffe [4].

The formula (9.28) for ψ_{VB} can be re-arranged as this:

$$\psi_{VB} = \sum_{k=1}^k a_k \Omega_k \quad (9.30)$$

where Ω_k is the sum of Slater determinants selected from (9.29) by their belonging to a certain valency scheme.

For a given set of valence atomic orbitals, each scheme is determined by the combination of atomic orbitals into pairs. Each pair of atomic orbitals χ_l, χ_m becomes a part of determinants of the corresponding structure in the form of combinations $\chi_l \bar{\chi}_m$ or $\chi_m \bar{\chi}_l$. Thus the function Ω_k of a certain valency structure corresponds to a certain scheme of distribution of electrons having spins α and β by the valence atomic orbitals; the valency dash, which binds atomic orbitals into pairs, corresponds to their population by electrons with opposite (paired) spins. Valency structure is the scheme of pairing of valency electrons.

Consider an example.

Two pairing schemes can be given for the configuration $abcd$:

$$\begin{array}{ccc} a-b & \text{and} & a & b \\ & & | & | \\ c-d & & c & d \end{array}$$

and using six Slater determinants we can construct two functions:

$$\begin{aligned} \Omega_{ab, cd} &= [\bar{a}b\bar{c}d] + [\bar{b}a\bar{c}d] + [\bar{a}b\bar{d}c] + [\bar{b}a\bar{d}c] \\ \Omega_{ac, bd} &= [\bar{a}c\bar{b}d] + [\bar{b}a\bar{c}d] + [\bar{a}b\bar{d}c] + [\bar{c}a\bar{d}b] \end{aligned}$$

It is evident that the function $\Omega_{ad, bc}$ corresponding to the structure $\begin{smallmatrix} a & b \\ c & d \end{smallmatrix}$ is a linear combination of the functions $\Omega_{ab, cd}$ and $\Omega_{ac, bd}$.

For configurations (9.27) and $S = 0$ we have $K = \frac{n!}{(n/2+1)!(n/2)!}$ independent valent structures (Rumer diagram) and $L = 2^{n/2}$ Slater determinants in each function Ω_k .

The selection of independent structures for a given electron configuration (9.27) is governed by the Rumer rule (see the book by Hellmann "Quantenchemie" [5]).

When we have constructed the functions Ω_k it only remains to find the coefficients a_k from the functional minimum condition

$$J_{VB}(\vec{R}; \tilde{\psi}_{VB}) = \int \tilde{\psi}_{VB}^* \hat{H} \tilde{\psi}_{VB} dv d\sigma \quad (9.31)$$

taking into consideration the additional condition

$$\int |\tilde{\psi}_{VB}|^2 dv d\sigma = 1 \quad (9.32)$$

Unlike the case with the molecular orbital method, the condition (9.32) is obligatory, because one-electron functions, from which Slater determinants are constructed, are not orthogonal. From (9.31), (9.32), and (9.30) we obtain the following system of linear uniform equations relative to the coefficients a_k :

$$\sum_{l=1}^K (H_{kl} - E\Lambda_{kl}) a_l = 0 \quad (k=1, 2, \dots, K) \quad (9.33)$$

and the equation

$$\sum_{k,l=1}^K \Lambda_{kl} a_k^* a_l = 1 \quad (9.34)$$

Here the integrals

$$H_{kl} = \int \Omega_k^* \hat{H} \Omega_l dv d\sigma \quad (9.35)$$

$$\Lambda_{kl} = \int \Omega_k^* \Omega_l dv d\sigma \quad (9.36)$$

can be regarded as the elements of the Hermitian matrix having the dimension of $K \times K$. Unlike the integrals F_{kl} and S_{kl} of the MO method, the integrals H_{kl} and Λ_{kl} of the VB method are many-electronic, i.e. the integration is done by the coordinates of all N electrons. By solving the system of equations (9.33)-(9.34) we obtain K values of the energies E_i and the corresponding sets of coefficients a_{ki} . The least root E_0 is the full energy approximation of the ground electron state, while the coefficients a_{k0} determine the function ψ_{VB}^0 of this state. Simultaneously obtained values of E_i for $i > 0$ correspond to the energies of excited electron states. It should be noted that in the VB method we obtain at once the full energy and the many-electron wave function without intermediate one-electron characteristics, and the selection of the values of E_i is not difficult. This is the general picture of the valence bond method.

This method has been developing in the following two directions:

- (1) verification of the theory by increasing the number of configurations (along with the covalent configuration of ionic members);
- (2) simplification of the method by reducing the number of valency schemes (often to one scheme); this approach has been used to substantiate the concept of hybridization of atomic orbitals. This is the subject of our discussion in the next paragraph, while here we shall briefly consider the problem connected with the improvement of the valence bond method.

The main disadvantage of the function ψ_{VB} corresponding to one covalent* configuration is that such a function gives an incorrect

* i.e., configurations of neutral atoms.

picture of distribution of the electron density; for example, the dipole moment calculated with the help of such a function appears to be equal to zero. This makes the described scheme of the VB method inapplicable to systems with sharply non-uniform distribution of the electron density (charge transfer complexes, coordination compounds, systems with the hydrogen bond, and simply molecules with great dipole moments). The wave function can in this case be improved by including the members corresponding to one or several ionic configurations into the ψ_{VB} . This is necessary to calculate the energies E_i and functions of the lower excited electron states*.

Consider another example, where one configuration is, in principle, insufficient to construct ψ_{VB} . These are homonuclear molecules with an odd number of electrons. The wave function of the system He_2^+ should be constructed with two configurations of equal weight: $(a1s)^2 2s(b1s)^2$ and $(a1s)^2 (b1s)^2 2s$. In this connection it should be noted that the wave function

$$\psi = \frac{1}{\sqrt{2(1+S_{ab})}} [\chi_a + \chi_b]$$

of the molecular ion of hydrogen can equally be regarded as ψ_{MO} and as ψ_{VB} . The difference between the MO (LCAO) and VB methods begins when systems with two and more electrons are involved.

Comparison of non-empirical MO (LCAO) and VB methods. Consider two problems: (1) comparison of wave functions ψ_{MO} and ψ_{VB} using a two-electron system as an example; (2) comparison of calculation techniques in the MO (LCAO) and VB methods.

It is reasonable to compare wave functions of various methods only for non-empirical variants of these methods, and ψ_{MO} and ψ_{VB} should be constructed with one and the same basis χ_k .

The books on quantum chemistry, "Valence" by Coulson [6] and "Valency Theory" by Murrell, Kettle, and Tedder [7], consider this problem using a hydrogen molecule as an example. Since the transition to more complicated systems does not give substantially new results the following general conclusions can be formulated:

(1) The Heitler-London method disregards the ionic members [i.e. the members of the type $\chi_a(1)$ and $\chi_a(2)$] in the wave function, while the MO (LCAO) method overestimates them.

(2) Because of the described special characteristics of ψ_{MO} and ψ_{VB} , the VB method accounts, to a certain degree, for the electron correlation, which explains the greater popularity of this method compared with the MO (LCAO) method, as related to the calculation of the physical characteristics which to a considerable extent depend on the correlation effects (e.g. the bond energy).

* Long-wave transitions in many polar molecules correspond to the so-called charge transfer band.

(3) The MO method is inapplicable to great interatomic distances, where the electron correlation becomes significant, and on the contrary, it is more advantageous than the VB method for close distances. It follows therefore that for non-empirical calculations of potential surfaces, which are mainly concerned with the behaviour of the wave function at medium distances (the region of activated complex) and at long distances (end products), the VB method should be preferred. This was pointed out by Coulson [6, p. 265] and has been proved by the modern calculations (e.g. see the book by Kaplan [8]).

Viewed in retrospect (before the 1950s) these two methods (MO and VB methods) were equally used in quantum-chemical calculations, but beginning with the 1950s the popularity of the molecular orbital method increases.

Suffice it to say that many books were published during the past decade in which the MO method is discussed in connection with the solution of various chemical problems (for example, Refs. [9], [10], [11], [12], [13]). And we cannot name a single book which was dedicated to the valence bond method during this period. The success of the molecular orbital method can be explained (among other reasons) by special features of its calculation procedures. Another cause, connected with the specificity of the simplest modifications of these methods, will be discussed in the next paragraph.

So, let us compare the MO (LCAO) and VB methods from the aspect of manual and automatic computing techniques. Take a system of N electrons and use one and the same set of AO's χ_k in both methods. Consider the calculating procedure by steps:

- (a) writing a general many-electron wave function;
- (b) calculation of matrix elements and calculation of the necessary molecular integrals;
- (c) solution of a system of equations.

The first problem is simple with the MO (LCAO) method. The entire information on ψ_{MO} can be written in the form of a matrix of coefficients C_{kp} having the dimensions $(N/2) m$. In the VB method, it is necessary to construct the wave function for each value of n . Of course, it is possible to make automatic the entire process by introducing the permutation matrices into the computer storage, but this is only practicable for a system with a comparatively small number of electrons.

In both methods, it is necessary to calculate the same molecular integrals, whose number and concrete magnitudes are determined only by the given atomic basis χ_k .

A system of non-linear equations (9.24) is usually solved in the Roothaan method by successive approximations: a starting matrix $\tilde{\mathbf{P}}^{(0)}$ is given and the matrix $\mathbf{F}^{(0)}$ is constructed with its aid; the system of equations (9.24) is then solved as a linear one, and the obtained set of coefficients is used to construct the matrix $\tilde{\mathbf{P}}^{(1)}$ in the next

approximation; then $F^{(1)}$ is constructed, etc., until self-consistent solutions are obtained (i.e. until $\tilde{P}^{(k)}$ coincides with $\tilde{P}^{(k-1)}$ to a certain preset accuracy). This process, as a rule, requires a great number of iterations (20 and over), and is inapplicable for manual calculations. At the same time the Roothaan method is convenient with computers because the matrices S and F are comparatively small [varying from $N/2$ to N ; see the condition (9.20)], and the procedure of self-coordination is not difficult for the computer.

The picture is different with the valence bond method. The system of equations (9.33) is linear and it should be solved by a single procedure. But if all valency schemes are taken into account for a given configuration (their number K rapidly grows with the increasing number of electrons), secular equations of the order

$$K = \frac{n!}{\left(\frac{n}{2} + 1\right)! \frac{n}{2}!}$$

should be solved. The VB method is convenient for systems with a small number of electrons [once the molecular integrals are known, it is not difficult to solve the system of equations (9.33)]. It is for this consideration that the valence bond method is used more often than the molecular orbital method in manual non-empirical calculations of separate molecules. But with $n = 20$, K is as great as 16,796(!) In order to make any practical use of the valence bond method, it is necessary to choose (artificially) from K schemes only a few most important ones. Intuition and experience help man to make the correct choice but a computer must be supplied with some criteria for such a choice to be made. Such criteria are however different in each case.

From what has been said, we can conclude that the MO method is more suitable for routine computations. Therefore, in nowadays, when manual calculations are used for training purposes only, or as a tribute to history, while quantum-chemical problems are being solved by computers, preference is universally given to the MO (LCAO) method.

3. Special Features of Semi-empirical MO (LCAO) and VB Methods

The general characteristics of semi-empirical methods. The importance of quantum chemistry for a modern chemist consists not only in that it can give numerical values of physical quantities; what is more important is that quantum chemistry can be used to give qualitative explanations to chemical regularities and their essence. But success of such undertakings depends on a correct choice of the

model which would reflect the essence of a given phenomenon without attaching undue importance to side aspects of minor significance. Such models are usually connected with rough semi-empirical methods. Consider an example. Let us assume that we are interested in the qualitative regularities of the rate of radical polymerization of some monomers having similar structures. Assume also that we can draw the necessary conclusions by comparing activation energies in the considered series, and assess π -electron contributions to this energy using the simplest version of the MO (LCAO) method (the Hückel method). Although connected with approximation to reality, this approach is very convenient for the case. It is not rational to use a more complicated quantum-chemical method to solve this problem, the more so that it can be incorrect since it will involve too much approximation (the determining factor is the activation energy; its assessment by π -electron energy of a small portion of the system is too approximate; there are no data on geometry of the activated complex). In other words, the choice of a particular method depends on a concrete problem, and if the problem is difficult, simplified calculation procedures are used which make it impossible to draw too categorical conclusions.

In the previous paragraph we have considered mathematical formulas and discussed the essence of non-empirical MO (LCAO) and VB methods. Now, as we proceed to semi-empirical variants of these methods, we can consider new approximations and clear out on what foundation the quantum-chemical concepts, arising directly from this or that simple method, are based.

The mathematical formalism of semi-empirical methods has the following characteristics:

(a) a non-empirical method scheme is taken as the basis of a semi-empirical method;

(b) as a rule, this scheme is simplified;

(c) empirical parameters are used; they are selected to meet particular requirements of the problem*.

The simplicity of calculation in semi-empirical methods makes the interpretation of the results vivid and illustrative, which attracts the chemical researcher. On the other hand, it is very difficult (and sometimes even impossible) to control the main sources of error by semi-empirical methods. For example, to explain this or that regularity, in many semi-empirical calculations it is not physical magnitude** (e.g. the reaction rate constant, the energy of the chemical bond breakdown) which is determined, but a certain quantum-chemical characteristic (e.g. charges on atoms, conjugation energy,

* Item (c) distinguishes semi-empirical methods from non-empirical ones: non-empirical methods are characterized by approximations, while semi-empirical by the set of parameters which are specific for each particular case.

** That is the magnitude which can be measured by a direct experiment.

etc.), which is correlated with the physical value in question. Such correlations are not as a rule scientifically founded, and comparison with experiment is the main argument in their favour.

In other problems, where semi-empirical methods are used for quantitative calculations of certain physical characteristics (geometry of molecules, dipole moments, electron transition energies, etc.), such methods, owing to specially selected parameters, often give better results than non-empirical methods. This can be explained as follows: since the parameters are specially selected for the determination of certain molecular characteristics, they can account indirectly for the effects which are not apparently included in the calculation scheme of the starting non-empirical method (for example, the correlations effects may be taken into consideration in the semi-empirical MO (LCAO) methods). For this reason, it is impossible to verify the semi-empirical methods with sets of parameters selected for another scheme, as we pass over to more complicated schemes.

So, the main advantage of the semi-empirical methods is their simplicity and graphicalness, and the main shortcoming is the lack of control of approximations and errors.

Now let us proceed to a more concrete problem, viz., the discussion of the semi-empirical MO (LCAO) and VB methods. We shall mainly discuss illustrative models and correlate quantum-chemical characteristics with chemical concepts, the mathematical aspects being involved as little as possible.

The studies of the electron structure and the properties of molecules by simple semi-empirical MO (LCAO) and VB methods made it possible to formulate the following methodological recommendations:

(1) it is reasonable to use the VB method to explain the geometry of molecules, the principle of "valency saturation" and directionality of bonds;

(2) the MO method should preferably be used to consider the regularities of the electron spectra and electron density distribution (and hence, to assess the molecule reactivity);

(3) simple versions of the MO (LCAO) method are more convenient to examine systems with odd numbers of electrons.

These are the questions that we shall discuss in the next paragraphs.

Perfect pairing approximation and description of the chemical bond in the simplest version of the VB method. Quantum-chemical literature usually refers to the VB method as a graphical way of describing chemical bonds in full agreement with the concepts of classical chemistry. The previous paragraph shows that the VB method does not possess such graphicalness but, on the contrary, it is cumbersome and inconvenient for any calculations. What does this "graphicalness" then mean? Graphical are understood the concepts originating

from the simplest version of the VB method, known in quantum chemistry as the perfect pairing approximation. In the given case, one configuration and one pairing scheme for this configuration are used to construct the wave function. Then, in the equation (9.30), we have only one term for ψ_{VB} and we need not determine any coefficients (except the normalization factor). In other words, the wave function of the molecule $\psi_{VB} = \Omega_0$ in the considered simplification can be constructed immediately, without any calculations (here Ω_0 is the function of the chosen valency scheme normalized by unity). If this function is a suitable approximation of the function ψ of the ground electron state of a stable system of nuclei and electrons (i.e. of a molecule), it is possible to say that it gives a quantum-chemical description of chemical bonds. With the perfect pairing approximation, we can, in fact, obtain sufficiently graphical concepts:

(a) only valency electrons take part in the formation of chemical bonds;

(b) the number of such electrons for each atom is determined by its spin-valency;

(c) the valency dash, describing the bond between two atoms, corresponds to two valency electrons (one electron from each atom) with opposite spins;

(d) the number of valency electrons for each atom is a definite quantity, and the composition of a molecule is therefore quite definite as well (the valency saturation principle);

(e) the directional characteristics of valency orbitals determine geometry of the molecule (valency directionality principle).

We can see that the number of valency electrons (spin-valencies) and the type of atomic orbitals populated with these electrons are very important in the given scheme. Spin-valencies of isolated atoms "fully enter" into the molecule and are transformed into the valencies of bound atoms. The situation is really quite simple and graphical but it can be acknowledged only on the condition that the scheme can be limited to one method of pairing of valency electrons. The following aspects should be considered in this connection.

Using one scheme for the construction of ψ_{VB} we assume the possibility of selection of optimum electron configurations for the starting atoms. Theory does not provide any reliable criteria for such a choice, and various configurations, and accordingly various spin-valencies of atoms, should therefore be considered. For example, the optimum electron configuration of the atom is not necessarily the configuration of the ground state, as is the case with nitrogen $N(2s^2 2p^3)$, oxygen $O(2s^2 2p^4)$, or fluorine $F(2s^2 2p^5)$, but it can also be the configuration corresponding to any closely located excited level, as is the case with carbon, $C(2s^2 2p^3)$. It is reasonable to use electron configurations not of neutral atoms but of ions to describe compounds with

the donor-acceptor bonds. For instance, the optimum electron configurations of boron and nitrogen atoms in the complex $\text{BF}_3\text{—NH}_3$ are $\text{B}^-(1s^2 2s^2 2p^3)$ and $\text{N}^+(1s^2 2s^2 2p^3)$ rather than the configurations $\text{B}(1s^2 2s^2 2p^2)$ and $\text{N}(1s^2 2s^2 2p^3)$. This gives a qualitative description of the donor-acceptor bond without involving the concept of the "transition" of unshared pairs of the electron donor onto the unoccupied orbitals of the acceptor. Dative bonds in Cu_2 are another example. Here the optimum electron configuration corresponds to the excited state $\text{Cu}(\text{KL}3s^2 3p^6 3d^9 4s^4 p)$ (spin-valency is three). The choice of a particular configuration, and hence of spin-valency, is concrete in each particular case, and of greater use in such cases are not theoretical speculations, but verified information on the composition of molecules, their geometry, and properties. The only "theoretical" criterion for the selection of the proper configuration is the energy criterion: mean energies of configurations should not be great.* As a rule, the set of possible configurations for a given element is limited by electron excitations in the outer shell of the atom. The range of possible configurations for the atoms of the second period is rather definite. For heavier atoms, the range of possible electron configurations, and hence of spin-valencies, is comparatively large. For example, the possible configurations $3s^2 3p^3$ and $3s 3p^3 3d$ for phosphorus and $3s^2 3p^4$, $3s^2 3p^3 3d$, and $3s 3p^3 3d^2$ for sulphur can be used to construct the functions ψ_{VB} of various molecules containing these elements. Different configurations of one and the same atom can be optimal for various molecules**.

Another condition for the applicability of the perfect pairing approximation is the selection of the optimal valence atomic orbitals, i.e. such atomic orbitals which can be used to construct the best function Ω_0 for the given configuration. Such orbitals are, generally speaking, linear combinations of s -, p -, and d -orbitals of atoms and are called hybrid orbitals. The inclusion of the hybrid orbitals into the VB method arises from the necessity to simplify this method. For example, it is not obligatory to use the hybrid atomic orbitals of carbon to calculate the CH_4 molecule by the VB method. But the calculation of this molecule for the basis of s -, p_x -, p_y -, p_z -orbitals would involve all 14 variants of electron pairing for the $2s^2 2p^3$ configuration of carbon. The transition to hybrid atomic orbitals narrows the choice to only one variant. What is the main principle of construction of hybrid atomic orbitals?

Assume the existence of "pure" s , p , d , etc. sets of atomic orbitals χ_k at each atomic centre. Assume also that the atomic orbital of each

* The zero point of the energy scale is the energy of the ground state of the atom.

** These problems are probably solved more adequately now. See Chapter 10.

centre can be linearly transformed through one another:

$$\chi'_k = \sum_l U_{kl} \chi_l \quad (9.37)$$

so that each new basis set χ'_k best of all provides the perfect pairing approximation. If we want an accurate solution of the problem, it is necessary to express the one-structure function $\psi_{VB} = \Omega_0$ through the elements of the matrix U ; further, by substituting $\Omega_0(U)$ in (9.31) we shall obtain the apparent expression of energy through the elements of this matrix and will have to find the optimal expression of the matrix U from the condition of the energy functional minimum:

$$E_{VB}(\tilde{U}) = \int \Omega_0^*(\tilde{U}) \hat{H} \Omega_0(\tilde{U}) dv d\sigma \quad (9.38)$$

But immense difficulties stand in the way of solving this problem, and we shall therefore take another way. Assume that a certain set of atomic orbitals for the given electron configuration meets the demands of the perfect pairing approximation. If we disregard some terms (for example, the atomic orbitals overlap integrals**), in the expression

$$E_{VB} = \int \Omega_0^* \hat{H} \Omega_0 dv d\sigma$$

then, for a system with a closed shell, it can be re-arranged as follows:

$$E_{VB} = E_{at} + \sum_{k,l} Q_{kl} + \sum_{\substack{u,l \\ \text{(paired)}}} \mathcal{K}_{kl} - \frac{1}{2} \sum_{\substack{k,l \\ \text{(unpaired)}}} \mathcal{K}_{kl} \quad (9.39)$$

The first term here is the sum of energies of isolated atoms; Q_{kl} and \mathcal{K}_{kl} are the "coulomb" and "exchange" integrals, determined for the pair of atomic orbitals χ_k and χ_l .

All pairs of atomic orbitals are summated in the first sum, and only pairs of atomic orbitals corresponding to the bond in the given pairing scheme in the second; the third sum includes pairs of non-bonded atomic orbitals. The expression (9.39) is called the *formula of perfect pairing*. Derivation of this formula cannot be considered theoretically grounded and it can therefore be used for calculations and assessments only on the condition that it is regarded as a semi-empirical formula, i.e. only after introducing into the integrals Q_{kl} and \mathcal{K}_{kl} , some parameters indirectly accounting for the terms which were omitted during its derivation. With such an approach, the

* That is, corresponding to a certain value of the quantum number "l".

** It is unlawful, because this is the atomic orbitals overlapping which is responsible for the presence in the expression (9.38) of a minimum at a certain nuclear configuration, i.e. it corresponds to a stable state (see, for example, Refs. [4] and [8]).

“exchange” integrals should be regarded as negative and approximately proportional to the squares of the overlap integrals S_{kl} *.

Hence we arrive at a conclusion that the energy of the system will be less (and the molecule will therefore be less stable) if the degree of overlapping of the atomic orbitals forming the bonds is greater, and if the degree of overlapping of the atomic orbitals not bound by valencies is smaller. Here arises the qualitative explanation of the equilibrated geometry of the molecule and the “substantiation” of the method for construction of hybrid orbitals: hybrid atomic orbitals should be mutually orthogonal and give the maximum overlapping of the orbitals forming the bond (for details see Ref. [15]). Well known sp^3 -, sp^2 -, and sp -hybrid orbitals of carbon, which are used for the qualitative description of the chemical bond in molecules of methane, ethylene, and acetylene, are the orbitals having such properties.

The concept of atomic orbital hybridization is widely used to explain various properties of molecules. In some cases the type of hybrid orbitals is found from the geometry of molecules (for example, the type of hybrid atomic orbitals of carbon is determined from the postulated property of their symmetry); and in other cases, on the contrary, the conjectured hybridization of atomic orbitals of the valency shell of atoms can be used to predict the geometry of molecules (Gillespie’s classification; see, for example, Ref. [16]). It should be noted, however, that geometry of a molecule *does not depend* on hybridization of atomic orbitals as some chemists try to represent it in a simplified form. The equilibrium geometry of a molecule is determined by any method from the energy minimum. If hybridization of atomic orbitals *reflects* the geometry of a molecule in the perfect pairing approximation, this concept can be used; otherwise (as is the case with the LCAO method) this concept is inapplicable.

Consider the problem of applicability of the perfect pairing approximation. This approximation becomes possible only if we can, for the given optimum configuration, introduce a basis χ_k in which the non-diagonal elements of the matrices \mathbf{H} and \mathbf{A} in equations (9.33) are small. Then, we can disregard these elements and obtain, instead of the system (9.33), separate equations for each energy level, i.e. expressions of the (9.39) type for each pairing scheme. The field of application of the perfect pairing approximation is determined by specificity of nuclear configuration and the electron structure of objects: as a rule, these are saturated hydrocarbons and their substitutive derivatives, and also some simple inorganic molecules having

* We do not give the explicit form of the integrals Q_{kl} and \mathcal{K}_{kl} (these can be found in many textbooks [6, 7]) for an unexperienced reader not to make wrong conclusions from them. For detailed mathematical aspects of the equation (9.39) see Ref. [14] (in connection with the discussion of the Hurley, Lennard-Jones and Pople method).

comparatively low symmetry and uniform distribution of electron density. But in many cases there are several energetically equivalent or close pairing schemes (i.e. several equivalent or similar diagonal elements of the matrix H). And it is impossible to remove this phenomenon by transition to another configuration or by selection of hybrid orbitals. It becomes necessary to solve a system of equations (9.33) for at least several (if not all K) main structures. This approximation of the VB method is known in quantum chemistry as the "structure resonance". An example is the π -electron structure of conjugated systems. A definite pairing scheme and the resultant effects, e.g. the descriptiveness of the valent dash, lose their sense with the resonance. Complex compounds are another example. Distribution of electron density in such systems is sharply non-uniform and the covalent configuration alone does not describe the properties of the electron structure of such objects. At the same time the ionic configuration alone gives too high formal charges on atoms. Good approximation of the wave function can in this case be obtained by constructing a linear combination of ionic and covalent structures. This approximation is known as the *ionic-covalent resonance*. The formula of perfect pairing does not hold here either, and the graphical concepts of the valency lines become senseless.

Some characteristics of semi-empirical LCAO methods. What attracts chemists to the most simplified semi-empirical method is that we can conclude on the structure and properties of molecules without calculating the wave function. The simplest VB method (the perfect pairing formula) has this attractive advantage. At the same time, it is not characteristic of the LCAO method. True, in some cases the coefficients of matrix C can be written from symmetry considerations (two-atom homonuclear molecules, π -electron system of benzene) but this is an exception rather than a rule. Moreover, the information on the orbital coefficients (without knowledge of the population and the relative arrangement of the corresponding one-electron levels) is insufficient even for qualitative consideration of the properties of molecules, while the values of these levels can be only calculated. Textbooks of quantum chemistry, as they discuss the MO method, using diatomic homonuclear molecules as examples, give the so-called "correlation diagrams" in which one-electron levels of isolated and bound atoms are compared. As we assess these diagrams from the modern aspects, we can feel their anachronism and the lack of direct importance as the source of information on the arrangement of one-electron levels of a molecule at an equilibrium internuclear distance. The value of these diagrams is that they are prototypes to the correlation Woodward-Hofmann rules (the conservation of the orbital symmetry in chemical reactions), which are widely used now in modern theoretical organic chemistry [(for details see Ref. [17]).

Thus any semi-empirical version of the LCAO method is characterized by definite (although quite similar) calculations which can practically be performed only by computers. Such calculations can give only qualitative information on the structure and properties of molecules. Homonuclear diatomic molecules are perhaps the only exception. The symmetry of these systems (the presence of the plane of symmetry, which is perpendicular to the molecule axis and passes between the nuclei) rigorously differentiates between bonding and antibonding molecular orbitals and the corresponding one-electron energies. Bonding molecular orbitals (φ_{bond}) are symmetrical functions relative to the reflection in said plane, and the antibonding orbitals ($\varphi_{\text{antibond}}$) are antisymmetric. In other words, if we assume a system of coordinates x, y, z , with the origin in the molecule centre, and the z -axis parallel to the axis of the molecule, then

$$\begin{aligned}\varphi_{\text{bond}}(x, y, -z) &= \varphi_{\text{bond}}(x, y, z) \\ \varphi_{\text{antibond}}(x, y, -z) &= -\varphi_{\text{antibond}}(x, y, z)\end{aligned}$$

It follows, in particular, that $\varphi_{\text{antibond}}(x, y, 0) = 0$, i.e. the plane $z = 0$ is the nodal plane for the antibonding molecular orbital. This problem is discussed in detail in [1, 6, 7]. The bonding and the antibonding molecular orbitals make it possible to formulate tentative rules which vividly explain the formation of the chemical bond and in some cases help draw conclusions about its strength.

(1) The chemical bond in a homonuclear diatomic molecule can be formed on the condition that the bonding molecular orbitals contain more electrons than the antibonding orbitals.

(2) As an electron is removed from a bonding (antibonding) molecular orbital, the chemical bond is weakened (strengthened).

This example of graphical presentation of the LCAO method is discussed in detail by Coulson [6] and Murrell [7]. These "rules" correlate the energy properties of molecules with their structure (see, e.g., Ref. [18]). In this connection we should like to mention the following. The formulated "rules" of the MO method, as well as the method itself, are tentative and not valid for all cases. This was noted by some authors [19] who considered molecules of the alkaline metals Li_2 , K_2 , Cs_2 , Rb_2 as examples. The chemical bond in them is less strong than in the corresponding cations, although the electron is removed from the bonding molecular orbital in these molecules. There may be several causes of this "violation" of the rule. But it is impossible to determine, without quantitative calculations, which of these causes is more important. This can be the disadvantage of the approximation of the MO method proper, disagreement between one-electron levels and full energies; one of the important causes

can be the considerable difference between one-electron levels and molecular orbitals of a neutral molecule and an ion*.

Before we go on to discuss polyatomic molecules it is necessary to note that we cannot speak about bonding and antibonding molecular orbitals in general when dealing with polyatomic molecules. We can only speak about the bonding and antibonding character of a given molecular orbital in the region of a given chemical bond. Symmetry of the molecular orbital is very important here. It is used not only for the study of spectral characteristics of molecules but also in the discussion of some chemical reactions. For instance, in addition to the Woodward-Hofmann rules [17] which are used, for example, in cycle-addition reactions of conjugated systems, we should like also to mention the Pearson symmetry rules. They can be used to predict the course of decomposition of symmetrical inorganic complexes (see Ref. [20]). Certain conclusions about the strength of bonds can in some cases be derived when considering the electron density matrix P_{kl} and multiplicity of bonds.*

But in the general case, the problem of strength of the chemical bond in polyatomic molecules is not at all trivial and requires consideration of at least the electron structure of the entire molecule rather than of its separate fragments.

It follows therefore that without quantitative calculations it is impossible to use the MO method even for qualitative conclusions. Many semi-empirical versions of the LCAO method have been recently developed. They are all claimed to be "methods" and much calculation work has been done, so that it becomes difficult to handle it freely even to an expert in the subject. The system of approximations and parameters, which distinguish one method from another, is discussed in detail by Dewar [13] and McWeeny and Sutcliffe [4]. We shall only dwell on some characteristic features of semi-empirical LCAO methods.

These methods usually deal only with a part of the electrons in a molecule (e.g. π -electron approximation, approximation of all valency electrons).

All these methods adhere to the main calculating procedure for the determination of the coefficients C_{kp} by solving the following:

$$\sum_{l=1}^n [f_{kl} - S_{kl}\epsilon_p] C_{lp} = 0 \quad (k = 1, 2, \dots, m) \quad (9.41)$$

on the condition of normalization of the equation (9.23) for each p^{***} . The system (9.41) resembles the Roothaan equation (9.24) and differs from it by the type of matrix elements.

* The latter is a system with an open shell.

** Bond multiplicity is the subject of our discussion in the next section.

*** There are also other versions of semi-empirical LCAO methods, e.g. those proposed by McWeeny [4] and Mestechkin [20].

The matrix elements f_{kl} are determined by simple evaluations and tentative formulas, and also contain empirical parameters, whose values are expressed through the characteristics of molecular fragments (e.g. atom ionization potentials, bond energies) or selected so that the given method should be adapted as much as possible to the calculation of concrete molecular characteristics.

The LCAO methods in question only differ in the system of approximations and selection of empirical parameters, and this makes them look similar. But these are the approximations and parameters that determine the field of application of a method with respect to both the object and the molecular characteristics to be calculated. We shall therefore discuss this question in more detail.

First of all let us consider the object of calculation. There exists an opinion that the MO method provides only very general approach to all chemical compounds. For example, Syrkin writes in his survey of the valency problem [12]: "The MO method is a generalization embracing all types of bond, from ionic to covalent, in one theory." It should be noted, however, that when Syrkin wrote about the universal character of the MO method (in the sense of selection of the object of calculation) and opposed the MO method to the VB method, he meant the simplest semi-empirical versions of both methods: the methods by Hückel, Pople, or Wolfsberg-Helmholtz (LCAO method) and the perfect pairing formula (VB method). Compared with the perfect pairing approximation, the simple MO methods have a larger field of application and are therefore more popular with chemists. But the main reason why the MO method has practically superseded the VB method is that the former is more convenient for routine computations.

Semi-empirical methods often widen the field of application of the MO method. Energy surfaces and profiles of the reaction coordinates for many complicated systems can be calculated with Complete Neglect of Differential Overlap (CNDO) and the Modified Intermediate Neglect of Differential Overlap (MINDO) methods*. There is a specially selected set of parameters of the CNDO method for the calculation of the depth and the shape of potential wells, and equilibrium distances of molecules. The realistic picture of the obtained results indicates operability of the semi-empirical methods for the calculation of characteristics which, being dependent on the electron correlation, cannot be handled with the non-empirical molecular orbital method. At the same time, the set of parameters developed for the calculation of certain physical values can be ineffective for the calculation of other values. For example, the Del Re method is used for the calculation of dipole moments and is completely useless to predict the energy characteristics of the molecule.

* For semi-empirical variants of the LCAO method see Ref. [13].

(strength of bond, force constants). The same holds for the objects of calculation: the Pople method, for example, is used to calculate organic molecules, and the Wolfsberg-Helmholtz method, for the calculation of inorganic complexes.

To summarize, it should be noted that the MO (LCAO) method is not at all universal with respect to the objects, or to the calculated characteristics. "Versatility" of the LCAO method consists in the following: if we investigate the store of the numerous semi-empirical modifications of this method, we can always choose a version optimal for the particular purpose. This wealth of the molecular-orbital models has resulted from numerous computer calculations, for which the LCAO method suits best of all. If we assess the possibilities of the semi-empirical MO (LCAO) and VB* methods from the aspect of the modern state of science, the latter seems to be "frozen", whereas the MO (LCAO) method is being constantly developed for various approximations and parameters. The VB method does not seem to be promising in this respect. This is so not because it is impossible to develop various semi-empirical variants which would widen substantially the possibilities of this method, but because it cannot be handled by computers. And the computer is an indispensable tool of the modern chemist. Graphical concepts and all kinds of speculations have outdated themselves. Quantum chemistry is now following a path of quantitative calculations and is becoming a science dealing with quantitative characteristics of electron structure of atoms and molecules.

References

1. Veselov, M. G., *Elementary Quantum Theory of Atoms and Molecules*, 2nd enl., ed., Fizmatgiz, Moscow, 1962 (in Russian).
2. Bersuker, I. B., *Structure and Properties of Coordination Compounds*, 2nd enl. and rev. edition, Khimia, Leningrad, 1976 (in Russian).
3. Tatevskii, V. M., *Classical Theory of Molecular Structure and Quantum Mechanics*, Khimia, Moscow, 1973 (in Russian).
4. McWeeny, R., Sutcliffe, B. T., *Methods of Molecular Quantum Mechanics*, Academic Press, London—N.-Y., 1969.
5. Hellmann, H., *Quantenchemie*, Denticke, 1937.
6. Coulson, C. A., *Valence*, Oxford, 1961.
7. Murrell, Y., Kettle, S. F. A., Tedder, J. M., *Valence Theory*, London-Sydney, 1965.
8. Kaplan, I. G., *Symmetry of Many-electron Systems*, Nauka, Moscow, 1969 (in Russian).
9. Straitwieser, *Molecular Orbital Theory*, John Wiley, 1961.
10. Pullman, B., Pullman, A., *Quantum Biochemistry*, Interscience, N.-Y.—London, 1963.
11. Bellhausen, C. J., *Ligand Field Theory*, McGraw-Hill, 1962.
12. Bazilevsky, M. V., *Molecular Orbital Methods and Reactivity of Organic Molecules*, Khimia, Moscow, 1969 (in Russian).

* Ionic configurations are considered whenever necessary.

13. Dewar, M., Dougherty, R. C., *The PMO Theory of Organic Chemistry*, Plenum-Roetta Edition, N.-Y., 1975.
14. Slater, J. C., *The Quantum Theory of Molecules and Solids*, I. Electron Structure of Molecules, McGraw-Hill, N. Y., 1963.
15. Syrkin, Ya. K., Dyatkina, M. E., *Chemical Bond and Molecular Structure*, Goskhimizdat, Moscow-Leningrad, 1946 (in Russian).
16. Gillespie, R. J., *J. Chem. Educ.*, 1970, p. 18-22.
17. Woodward, R. B., Hofmann, R., *The Conservation of Orbital Symmetry*, Academic Press., N.-Y., 1970.
18. Shchukarev, S. A., *Inorganic Chemistry*, vol. 1, Vysshaya Shkola, Moscow, 1970 (in Russian).
19. Yatsimirsky, K. B., *ZhVKhO im. Mendeleeva*, vol. 17, 1972 (in Russian).
20. Adamov, M. N., Borisova, N. P., in the book "Problems of Theoretical Physics", vol. 1, Leningrad University Press, 1974 (in Russian).
21. Syrkin, Ya. K., *Usp. khim.*, 1959, vol. 38, issue 8, p. 903-920 (in Russian).

Hypervalent Bonds in Coordination Compounds of the Main Sub-group Elements

1. Special Features of Electron Structure of Coordination Compounds of Non-transition Elements

Theoretical and experimental inorganic chemistry attaches great importance to the electron structure of compounds of the transition metals. Valence ($n - 1$) d -orbitals of the atoms of these elements are successively filled with electrons, whereas all np -orbitals remain vacant (at least in the ground state of the atom) and this determines the nature of complexes of the transition metals.

In the atoms of the elements of the main sub-groups, successively filled with electrons are the valence np -orbitals, while the nd -orbitals remain completely vacant which fact is undoubtedly the cause of distinct differences in the electron structure of complexes of the transition metals on the one hand, and of non-transition elements on the other hand. But despite these differences in the valency electron structure of isolated atoms of the transition and non-transition elements, the differences *apriori* indicating specific characteristics of the chemical bond in coordination compounds of non-transition elements, our knowledge of their nature and the electron structure has been and remains in many respects the result of an unfounded extension of the general ideas of the theory of structure of complexes of the transition metals to the description of chemical bonds in coordination compounds of the elements standing in the main sub-groups or, in other words, the result of the unfounded thesis of similarity and even identity (at least in the qualitative aspect) of the principles of the molecular structure of these two types of complexes.

The idea of hybridization of valence atomic orbitals is one of the most general, in its character, ideas in quantum-mechanical theory of molecular structure. The use of the concepts of hybridization of valence atomic orbitals, both in the case with the transition metal complexes and with non-transition element complexes, is always connected with the participation in the chemical bonds with ligands of not only occupied valence atomic orbitals [ns and $(n - 1) d$ for the atoms of the transition metals and ns and np for the atoms of non-transition elements] but also of virtual atomic orbitals (np and nd respectively) not filled with electrons in the ground state of the central atom. Thus, the generally accepted interpretation of the electron structure of octahedral molecules MoF_6 and SF_6 (and naturally the explanation of all properties inherent in them) arises from the following assumption. Each molecule contains six M—F or E—F σ -bonds

formed with participation of the valence sp^3d^2 -orbitals of the central atom; in the theory of molecular orbitals they can be considered approximately as localized (two-centre) two-electron interactions of the central atom with the ligand. This can be compared with the statement that σ -bonds in such molecules are formed with the obligatory appearance of electrons in the valent state of the central atom in formerly vacant np -orbitals (in the complex of the transition metal Mo) or nd -orbitals (in the complex of non-transition element S).

The model of hybridization of valence orbitals of the central atom gives the traditional explanation to the most important properties of chemical elements of the second period as compared with the other elements of the main sub-groups (first of all we mean the appearance of energetically stable compounds at the highest stages of oxidation of non-transition elements of the third, fourth, fifth, and partly sixth periods, realization of great coordination numbers in their compounds, AsF_5 , ClF_5 , SiF_6^{2-} , PF_6^{1-} , SF_6 , IF_7 , SnF_8^{2-} , etc.). This model seems to give the proper interpretation of stereochemistry of molecules in direct connection with their electron structure [1, 2] and of some other important postulates of chemistry of elements of the main sub-groups.

Unfortunately, the situation, which at first sight seems quite advantageous for theoretical inorganic chemistry, becomes much complicated by the fact that while the participation of the virtual np -orbitals of the central atom in the formation of chemical bonds in transition metal complexes is theoretically grounded and verified experimentally, the participation of the virtual nd -orbitals of the central atom in the bonding with the ligands in coordination compounds of non-transition elements has never been reliably proved. Moreover, much evidence has recently been obtained which gives a different picture: the contribution of the ns -, np -, and nd -orbitals of the atoms of non-transition elements to the bonding with the ligands is quite varied and the decisive role in the formation of chemical bonds belongs to the np -orbitals of the central atom, while the role of the ns - and especially nd -orbitals is much less significant.

Despite the grounded differences in the results of non-empirical quantum-mechanical calculations of the electron structure of transition metal complexes, and also in the results of their X-ray structural analysis, the general character of conclusions about the participation of the virtual np -orbitals of the central atom in the bonding with the ligands is uniform and does not seem to be disputable. Some authors also indicate: the very fact that the empirical Sidgwick rule of the 18-electron shell holds for many transition metal complexes [at least the valency shell of the central atom contains much more than 12 electrons corresponding to complete population of six bonding molecular orbitals with participation of one ns - and

five $(n - 1)d$ atomic orbitals] definitely indicates the participation of not only ns - and $(n - 1)d$ -, but also np -orbitals of the central atom of these complexes in the formation of bonds with the ligands.

All this has predetermined the high interest in the study of the nature of coordination compounds of the elements of the main subgroups and gave a new impetus to the theoretical and experimental studies of their electron structure [3].

Kant said: "Each science contains as much of truth, as much mathematics is contained in it." But even if we do not take this saying of the philosopher as something absolute, we must admit that only complete and rigorous quantitative calculations can be regarded as sufficiently informative to enable us to derive conclusions about the nature of electron interactions in molecules of coordination compounds. Such calculations are one of the main methods of studying the discussed molecular systems, and the importance of the theoretical approach consists in that it helps us solve the problems which cannot be solved experimentally. The only theoretical methods suitable for attaining these objects are at the present time the analytical non-empirical method by Hartree-Roothaan-Fock (*ab initio* SCF* LCAO) and especially SCF SW X_α ** method by Slater and Johnson, which has certain advantages (essential in the analysis of contribution of the virtual atomic orbitals to the formation of chemical bonds) over the formalism of the LCAO method.

The approach to experimental methods should probably be the same rigorous. Among the new physical methods of studying the electron structure of molecules the main role belongs to the group of the electron spectroscopy methods. Using them in the experimental study of the nature of molecules reliably establishes the most important quantum-chemical characteristics of their electron structure: one-electron energies of the molecular orbitals, their population, contributions of basis atomic orbitals to molecular orbitals, and others. And therefore only those conclusions about the electron structure of molecules can be considered reliable which arise both from the results of complete SCF calculations, and from the experimental results of electron spectroscopic studies of the nature of molecules.

Recent SCF SW X_α calculations of several coordination compounds of non-transition elements (SF_6 , SeF_6 , TeF_6 , SO_4^{2-} [3, 4]) indicate that the virtual nd -orbitals of the central atom remain practically vacant during the formation of bonds with the ligands. Recent non-empirical SCF LCAO calculations of the same or similar molecules (SF_6 , PF_5 , ClO_4^{1-} [3, 5, 6]) give similar population pictures (though these results are not always clear because of variations in the scheme

* SCF—self-consistent field.

** SCF SW—self-consistent field of scattered waves in the basis X_α .

of filling of the electron shells) and indicate, on the whole, rather insignificant electron population of the *nd*-orbitals of the central atom.

Table 15 gives the results of calculations of the electron structure of the SF₆ molecule obtained by the SCF SW X_α and SCF LCAO methods; they are compared with the results of the experimental study of SF₆ by the electron spectroscopy methods for chemical analysis.

The similarity of the calculated (especially by the SCF SW X_α method) and the measured values is a reliable guarantee of correctness of all theoretically calculated characteristics of the electron structure of SF₆. These characteristics are as follows: of the 48 valency electrons in the SF₆ molecule, twelve are pseudoatomic and are localized in pairs in the 2s-orbitals of the fluorine atoms. Another 28 electrons occupy practically non-bonding molecular orbitals; their energies are somewhat different because of the inter-ligand interactions and only eight (not twelve) electrons occupy σ-bonding molecular orbitals *t*_{2u} and *a*_{1σ}. These molecular orbitals are only formed by the interaction of 2*p*_σ-orbitals of fluorine atoms and 3*s*- and 3*p*-orbitals of the sulphur atom, while the 3*d*_σ-orbitals of the sulphur atom do not contribute anything to these orbitals. The only σ-orbitals of the molecule into which the 3*d*_σ-orbitals of the atom S — *e*_g could make a significant contribution (by symmetry), remain

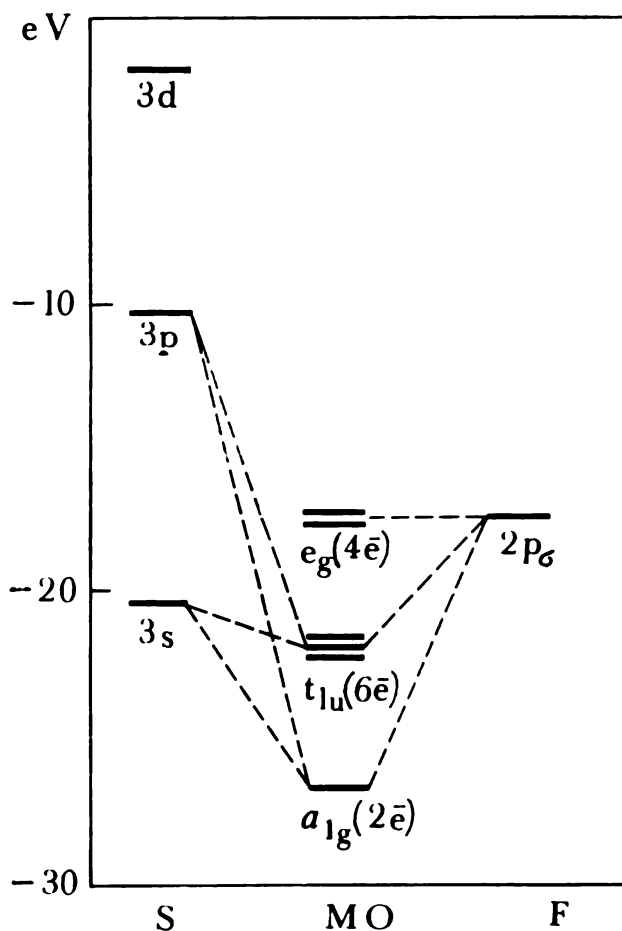
Table 15. Symmetry and One-electron Energies (eV) of Molecular Orbitals of SF₆ Molecule

MO of SF ₆			Orbital energies, eV		
			SCF SW X _α	SCF LCAO (<i>ab initio</i>)	ESCA
Antibonding	<i>t</i> _{1g} (π)	6e ⁻	-15.9	-18.2	-15.7
	<i>t</i> _{1u} (π)	6e ⁻	-16.8	-19.0	-17.3
	<i>t</i> _{2u} (π)	6e ⁻	-16.8	-19.4	-17.3
	<i>e</i> _g (σ)	4e ⁻	-17.5	-19.4	-18.7
	<i>t</i> _{2g} (π)	6e ⁻	-18.8	-22.2	-19.9
Bonding	<i>t</i> _{1u} (σ)	6e ⁻	-21.8	-24.7	-22.9
	<i>a</i> _{1g} (σ)	2e ⁻	-26.7	-29.6	-27.0
2s — F					
		4e ⁻	-35.6	-45.3	-39.3
		6e ⁻	-36.5	-46.8	-41.2
		2e ⁻	-39.3	-50.4	-44.2

substantially $2p_\sigma$ -orbitals of the fluorine atoms and they are therefore non-bonding in character. This indicates that $3d_\sigma$ -orbitals of the sulphur atom do not take appreciable part in the σ -bonding with the ligands. Thus, the bonds in the SF_6 molecule are ensured practically only by filling valency electrons into the σ -bonding molecular orbitals having the symmetry t_{1u} and a_{1g} , i.e. mainly by valency np - and partly ns -electrons of the central atom (Fig. 2).

Calculations show that bonding in molecules similar to SF_6 can be effected without π -electrons of the ligands as well. Nevertheless, in rigorous discussion of the electron structure of such molecules, we should not disregard the possible participation of the ligand π -electrons even in cases with monofunctional ligands, which in our case are the fluorine atoms. On the whole non-bonding π -orbitals t_{2g} of the SF_6 molecule are approximately 2 eV lower than the other non-bonding molecular orbitals. This probably shows a slightly bonding character of the t_{2g} -molecular orbital because of the small contribution of the $3d_\pi$ -orbitals of the sulphur atom. (The calculations show that the energy of the only molecular π -orbital t_{2g} , to which the $3d_\pi$ -orbitals of the central atom could contribute by symmetry, practically does not depend on the involvement of the $3d_\pi$ -orbitals

Fig. 2. Energy of atomic σ -orbitals of sulphur and fluorine, and molecular orbitals of SF_6 (atomic π -orbitals of fluorine and the corresponding quasi-atomic molecular orbitals of SF_6 are not shown).



of the sulphur atom.) In other words, this indicates that the π -bond between the central atom and the ligand is negligibly small. It is quite natural for molecules like SF_6 , because the π -bonds can in principle be formed exclusively by the donor-acceptor interaction $3d_\pi(\text{S})-2p_\pi(\text{F})$, which must be very weak.

Thus, the molecules in question always have non-bonding ligand orbitals characterized by the symmetry which is necessary for their interaction with virtual nd -orbitals of the central atom not occupied by the electrons. But the most complete quantitative calculations by the SCF LCAO method positively show that, except the orbitals which have the symmetry required for mixing with the nd -orbitals of the central atom, and whose energies are only insignificantly reduced by the incorporation of the nd -orbitals of the central atom, the energies of all other one-electron molecular orbitals (in consideration of the nd -orbitals of the central atom) increase. And although involvement of these nd -orbitals, in accordance with the variation principle, decreases the full SCF energy of the molecule, this is explained not by stabilization of one-electron orbitals (i.e. by decreasing overall orbital energy), but by the effects of a higher order, *viz.*, by the change in the Coulomb and the exchange interelectronic effects energy. Moreover, this lowering in the full energy of the molecule, due to involvement of the nd -orbitals of the central atom in the bonding with the ligands, is negligible and does not exceed 10^{-4} of the full energy (E) for all studied molecules (SF_6 , PF_5 , ClO_4^{1-} , and others). Strange as it may seem, this can be compared with the lowering of the full SCF energy of Ne atom due to the involvement of the g - and h -orbitals. It is clear therefore that the nd -orbitals of the central atom are really not important in the formation of bonds (first of all of σ -bonds) with ligands in non-transition element complexes. The full energy lowering due to the described effect of the involvement of the nd -orbitals is so small that with the same certainty we might as well speak about the participation of f - or g -orbitals of the central atom in the formation of bonds with ligands in octahedral complexes similar to SF_6 . These orbitals also might contribute to the t_{1u} and a_{1g} molecular orbitals and thus decrease the full energy of the molecule [5]. It is clear therefore that it is not at all necessary to involve the nd -orbitals of the central atom in the σ -bonding with ligands, and the role played by these virtual orbitals in the discussed molecules differs only insignificantly from the role played by other small corrections, such as the enlargement of the basis, contributions of the atomic orbitals characterized by even higher angular momentum, etc.

Thus, the only reliable results of theoretical and experimental investigation of the electron structure of the most typical coordination compounds of the elements standing in the main sub-groups give us grounds to draw a conclusion about the untenability of the

model of hybridization of the central atom valence orbitals (with obligatory participation of its virtual nd -orbitals) which is regarded as the general basis of the molecular structure of such complexes. Simultaneously, these results enable us to formulate such a generalized concept of molecular structure of non-transition element complexes which, in contrast to the former approach, would be completely adequate to their nature and would give a *similar in manner* explanation of as much experimental data as possible.

2. Hypervalent Bond Model

The new theoretical concept of the electron structure of molecules of non-transition elements standing in the 5-8th groups in their highest valency states was created comparatively not long ago [3, 5-11]. Its elaboration was based on the theory of four-electron three-centre bonds (and its more complicated modifications for five- and six-coordination molecular systems) which is now universally accepted as an alternative of the traditional theory of hybridization of valence $sp^m d^n$ -orbitals of the central atom.

In the pioneering work by Musher [7] the hypervalent bond theory is developed on the basis of the concepts of localized molecular orbitals. Since the bonds between the central atom and the ligand in the molecules of non-transition elements cannot be common two-centre two-electron bonds because of the inactivity of the nd -orbitals of the central atom, they are best of all (and in the simplest way) described in the terms of localized orbitals (using only np - and ns -valency electrons of the central atom) of three types.

The 1st type. Covalent (CV) two-electron two-centre bonds in each of which the valence np -orbital of the central atom, occupied by an unpaired electron, interacts with the valence atomic orbital of the ligand occupied by an unpaired electron. The molecular-orbital description of this interaction involves one occupied bonding

$$\varphi_1 \approx \chi_A + \chi_L \quad (2e^-)$$

and one vacant antibonding

$$\varphi_2 \approx \chi_A - \chi_L \quad (0e^-)$$

molecular orbitals. The bonds in the molecules ClF , SF_2 , PF_3 , ClF_2^{1+} , SF_3^{1+} , and PF_4^{1+} are examples of such bonds.

The 2nd type. Hypervalent-1 (HV-1) four-electron three-centre bonds, in each of which the valence np^2 -orbital of the central atom, occupied by an unshared electron pair, interacts simultaneously with two valence atomic orbitals of two "colinear" ligands, occupied with unpaired electrons. The molecular-orbital description of this bond

involves one occupied bonding

$$\varphi_1 \approx \chi_{L(1)} + \chi_A + \chi_{L(2)} \quad (2e^-)$$

one occupied non-bonding

$$\varphi_2 \approx \chi_{L(1)} - \chi_{L(2)} \quad (2e^-)$$

and one vacant antibonding

$$\varphi_3 \approx \chi_{L(1)} - \chi_A + \chi_{L(2)} \quad (0e^-)$$

molecular orbitals. Examples of such bonds are the bonds in the following molecules: XeF_2 , XeF_4 , XeF_6 , ClF_2^{1-} , ClF_4^{1-} , and IF_6^{1-} . Since four electrons in the linear fragment $\text{F}(1)-\text{A}-\text{F}(2)$ can be accommodated in the bonding φ_1 and non-bonding φ_2 molecular orbitals without involving the antibonding φ_3 -molecular orbital, the A—F bonds are on the whole rather strong (in XeF_2 , for example, it is as high as 30 kcal).

The 3rd type. Hypervalent-2 (HV-2) bonds. To form these bonds, the central atom, which in this case shows its highest valency, supplies not only its valence np -orbitals, but also the valence ns^2 -orbital occupied by an unshared electron pair. Thus, the hypervalent-2 bonds are three-centre four-electron bonds of the previous type but strengthened by the contribution of the ns -orbital of the central atom. True, the localized bonding molecular orbitals are not in this case directed along the Cartesian np -orbitals of the central atom, as is the case with the hypervalent-1 bonds. The participation of the ns -orbitals ensures the most symmetrical (of all possible) geometry of the molecule. The examples of the bonds are those in IF_7 , SF_6 , PF_5 molecules.

The special features of the hypervalent bonds of both types are their correspondence to the electron filling of not only the bonding molecular orbitals (which is typical of the ordinary covalent bonds) but also the corresponding non-bonding molecular orbitals (Fig. 3).

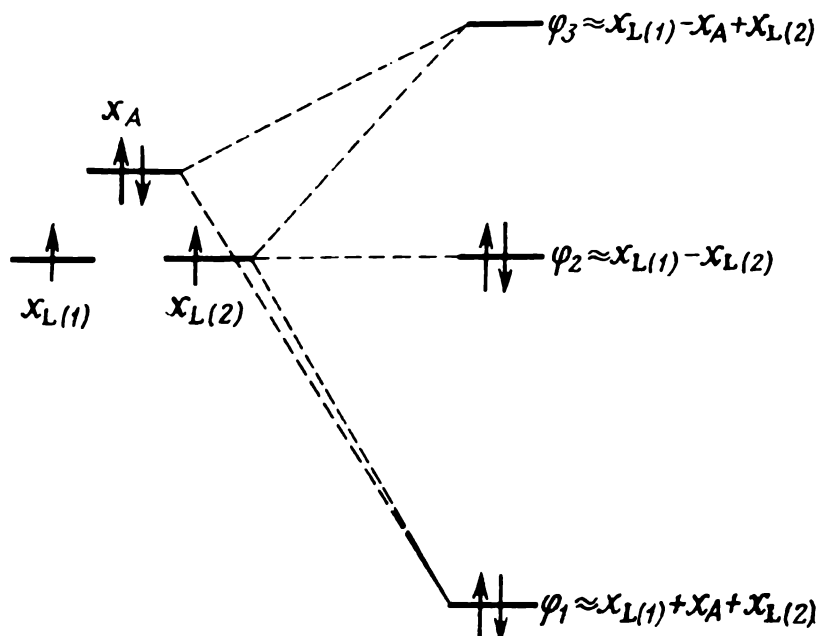
The relative contribution of the bonding molecular orbitals to the full energy of molecules, and hence to the strength of bonds, increases in the series hypervalent-1 < hypervalent-2 < covalent bond ($E_{HV-1} < E_{HV-2} < E_{CV}$). This explains all observed regularities in the internuclear distances A—L, the energies of the two-centre bonds A—L, and many other characteristics of these bonds in the molecules in question. Musher [7] indicates that the relative strength of all these bonds is as follows: the covalent bond is stronger than a half of the three-centre hypervalent-1 bond because the former involves only two bonding electrons, while *two* hypervalent-1 bonds involve two bonding and two non-bonding electrons; the latter decrease the energy of interaction by the additional inter-electron repulsion. The strength of the hypervalent-2 bond is intermediate,

because it is strengthened by the participation of two ns^2 -electrons of the central atom.

An important criterion of stability of hypervalent bonds is that its central atom must be sufficiently "electropositive" to give its np^2 - and even ns^2 -electron pairs to form bonds with ligands, while the ligands must be sufficiently "electronegative" to attract these electrons. But we now discuss only relative characteristics and that the general electron charge transfer during the formation of such bonds is not necessarily effected in the indicated direction ($A \rightarrow L$).

During the formation of four-electron hypervalent bonds in a linear three-centre fragment $L(1)-A-L(2)$, one electron pair occupies a non-bonding molecular orbital φ_2 (in the ground state, these were two unpaired electrons, $\chi_{L(1)}^1$ and $\chi_{L(2)}^2$, one electron in two ligands), and the electron charge thus remains localized on the ligands; the second electron pair occupies the bonding molecular orbital φ_1 and is thus delocalized between all three atoms of the fragment (in the ground state this electron pair χ_A^2 entirely belonged to the central atom). Thus, population of the molecular orbitals φ_1 and φ_2 in the linear fragment $L(1)-A-L(2)$ with electrons corresponds to the dislocation of the electron density from the central atom onto the ligands. Only strongly electronegative atoms (F, O, etc.) can therefore be ligands. Since the central atom acts as a donor of electrons, the strength of hypervalent bonds should in the general case decrease with the increasing ionization potential of the central atom. This, by the way, explains the existence of many stable fluorides, oxides, and oxyfluorides of xenon, whereas only one difluoride is obtained

Fig. 3. Molecular orbitals for three-centre four-electron interaction in the linear fragment $L(1)-A-L(2)$.

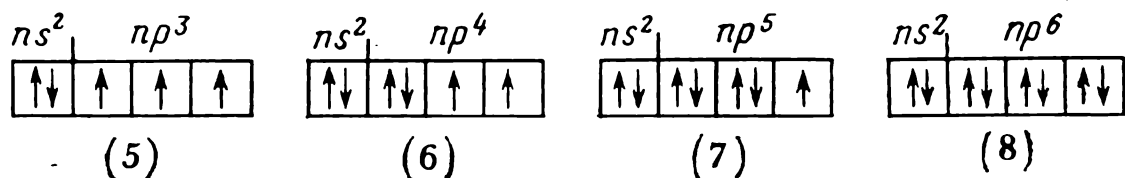


for krypton, and no stable chemical compounds are known for argon, neon, and helium whatsoever.

Thus, it is clear that multi-centre hypervalent bonds in molecules of non-transition elements of the 5-8th groups of the Periodic system arise each time when the number of bonds formed by the central atom is greater than the number of its valence np -orbitals, available for the formation of covalent bonds with ligands; and hypervalent bonds always arise in all cases where the central atom develops (increases) its valency to form bonds with a greater number of ligands, i.e. it has a greater coordination number compared with the total number of the valence np -orbitals. The orbital-deficient (the former term "excess electron") molecules are thus formed. The valency electrons should occupy in their electron structure the high non-bonding molecular orbitals localized exclusively on ligands. For this reason, the bonds in these molecules (SF_6 , SF_4 , PF_5 , ClF_5 , ClF_3) are weaker than in their analogues with lower valency of the central atom (ClF , SF_2 , PF_3). As viewed from the standpoints of the theory of molecular orbitals, the bonds in the orbital-deficient molecules arise from the cleavage between the corresponding bonding and non-bonding molecular orbitals and require re-distribution of the electron charge from the central atom onto the ligands, hence the high electronegativity of the ligands and, accordingly, electropositivity of the central atom. Multi-centre bonds are universal but they are formed only when the nature of the central atom and the ligands meets these requirements.

The role played by the valence ns^2 -electrons of the central atom in molecules with hypervalent bonds consists in decreasing the molecular energy when the ns^2 -orbital of the central atom, occupied by two electrons, is mixed with a suitable (with respect to symmetry) non-bonding orbital of the ligands, so that the electrons fill the resultant bonding and non-bonding molecular orbitals. But even the qualitative nature of such an interaction depends on a particular situation: the ns^2 -orbital of the central atom can be strongly mixed and can play a decisive role in the molecular stability (SF_6 , PF_5 , IF_7); on the other hand, the ns^2 -orbital of the central atom can be mixed weakly and its contribution to the bonding with ligands will be insignificant; for example, molecules XeF_6 , IF_5 , SF_4 have no bonding molecular orbitals involving the ns^2 -orbitals (the corresponding molecular orbitals have substantially non-bonding character). Thus, there is an essential difference between the two types of hypervalent molecules. The molecular-orbital approach, which "mixes", without sufficient grounds, all valence orbitals of the central atom, the ns -orbitals included, having in view only their symmetry characteristics, often gives an incorrect picture of the role that the ns^2 -electrons of the central atom play in the formation of bonds with ligands in higher molecules of non-transition elements.

The valency electron shells of atoms of non-transition elements of the 5-8th groups can schematically be represented as follows:



In the fluorides of the noble gases AF_2 , AF_4 , and AF_6 (8th group, by convention), all bonds of the central atom with the ligands arise from the four-electron three-centre interactions described above, and are hypervalent-1. The picture is completely the same with the interhalogen anions, IF_2^{1-} , IF_4^{1-} , and IF_6^{1-} , which are isoelectronic with the corresponding fluorides of xenon. All these molecular structures are characterized by strict linearity of its fragments $F_{(1)}-A-F_{(2)}$. For this reason, the molecules AF_2 are linear, AF_4 have plane-square conformation, AF_6 are octahedral; all A—F bonds are equivalent in all molecules.

In neutral molecules of the interhalogen compounds AF_3 and AF_5 , one A—F bond is always an ordinary covalent two-electron two-centre bond, the remaining bonds being four-electron three-centre hypervalent-1 bonds in linear fragments $F_{(1)}-A-F_{(2)}$. The molecules AF_3 have therefore T-shape structure, while the AF_5 molecules are tetragonal bipyramids. The internuclear distances in the linear fragments $F_{(1)}-A-F_{(2)}$ in each of these molecules are longer than in the only covalent bond A—F. The molecular fluoride anions SF_3^{1-} , SeF_3^{1-} , TeF_3^{1-} , SF_5^{1-} , SeF_5^{1-} , TeF_5^{1-} , etc., which are isoelectronic to the neutral molecules of the interhalogens, have the same structure.

In the SF_4 , SeF_4 , and TeF_4 molecules, and in their isoelectronic anions PF_4^{1-} , AsF_4^{1-} , and SbF_4^{1-} , two equatorial bonds A—F are ordinary covalent bonds, while the other two (apical) arise as a result of the formation of hypervalent-1 bond in the linear fragment $F_{(1)}-A-F_{(2)}$, at the expense of the only unshared electron pair in the valence np -orbital of the central atom. Such molecules have therefore the configuration of a swing with shortened equatorial bonds A—F.

Hypervalent-2 bonds are formed in molecules of non-transition elements with the highest valency of the central atom (IF_7 , SF_6 , PF_5). The valence ns^2 -orbitals occupied by two electrons take part in the formation of these bonds. The spatial arrangement of the ligands in such molecules satisfies the minimum energy condition of the interligand repulsion. The PF_5 molecule is therefore a trigonal bipyramid, SF_6 is an octahedron, and IF_7 is a pentagonal bipyramid. As a rule, the A—F bonds in such molecules and in their isoelectronic molecular ions (ClF_6^{1+} , PF_6^{1-} , SF_5^{1+}) have equal characteristics. This concerns, in the first instance, octahedral molecules AF_6 , where all A—F bonds are characterized by equal energies and internuclear distances.

Thus, the consideration of the IF_7 , SF_6 , and PF_5 molecules shows that their geometrical structure (D_{5h} , O_h , D_{3h}) does not depend on the participation of nd -orbitals of the central atom in the formation of bonds with the ligands, i.e. without the corresponding hybridization d^3sp^3 , d^2sp^3 , dsp^3 of its valence orbitals.

A more detailed discussion of stereochemistry of coordination compounds of non-transition elements can be found in special literature.

To end this paragraph, we should like to make some notes. The model, or rather the theory of hypervalent bonds, utilizes to the full extent one of the most general and fundamental concepts of quantum-mechanical theory of the chemical bond, which consists in that the prerequisite condition for an effective bonding (i.e. electronic interaction) of valence orbital of the central atom and the ligands is closeness of their orbital energies, which also explains why covalent bonds, arising from the interaction of unpaired electrons, are usually much stronger than the donor-acceptor and dative bonds. And this determines the degree of mixing of the interacting valence orbitals of the central atom and the ligands, namely: the closer the energies of the orbitals, the higher is the degree of mixing of χ_A and χ_L .

The stabilization energy of the bonding molecular orbital

$$\varphi = c_A \chi_A + c_L \chi_L$$

is expressed in the perturbation theory as follows:

$$\Delta E_{AL} \sim \frac{\beta_{AL}^2}{|\alpha_A - \alpha_L|}$$

where α_A , α_L are Coulomb integrals expressing the "self-consistent" energies of the orbitals χ_A and χ_L (in those approximations of the MO theory where the effective one-electron Hamiltonian is used), β_{AL} is the resonance integral expressing the energy of interaction of the orbitals χ_A and χ_L which is proportional to the overlap integral S_{AL} .

The differences in the energies of valence $(n-1)d$ -, ns -, and np -orbitals of the transition metal atoms are comparatively small (5-7 eV), and this explains the participation of all these valence orbitals* in the M—L bonds to justify the concept of hybridization of the valent atomic orbitals of the central atom in the theory of structure of molecules incorporating the transition metal atoms. The energies of the nd -orbitals of non-transition element atoms are 10-15 eV higher, and the energy of the ns -orbitals is 10-20 eV lower than the energies of the most important (for the bond with the ligands) valence np -orbitals. In other words, the energies of nd — np and np — ns

* Of course, when it is necessary.

separation in the non-transition element atoms are high and often exceed 10 eV (non-transition elements of the 5-8th groups of the Periodic system are meant). These energies increase with the number of the group. The energies of the valence orbitals of typical ligands are as a rule somewhat lower than the energies of the valence np -orbitals of the atoms of the elements standing in the main sub-groups of the 5-8th groups, and it is therefore clear that during the formation of molecules of coordination compounds of non-transition elements, the energies of the vacant nd -orbitals of the central atom are too high and nd -orbitals cannot interact with the valence orbitals of the ligands filled with electrons. For the same reason, the valence ns^2 -electrons of the central atom are not always effectively involved in the bonding with the ligands: their orbital energy is often too low compared with the energy of the valence orbitals of the ligands. What was said above makes evident the untenability of the concept of hybridization of the valence orbitals of the central atom (the more so with the involvement of its virtual nd -orbitals) during description of the most important characteristics of the electron structure of coordination compounds of non-transition elements and simultaneously emphasizes the universal character of the concepts of four-electron three-centre bonds in the orbital-deficient molecules, the concept which was first formulated and then developed in Refs. [3, 10, 11].

3. Chemical Consequences of Hypervalent Bond Model

The hypervalent bond model not only interprets stereochemistry of coordination compounds of the elements standing in the main sub-groups, but can also explain, and even predict, various characteristics of two-centre bonds A—L (energy, internuclear distance, etc.) in one and the same molecule. Consider several known fluorides of chlorine where the mean energy of the Cl—F bond decreases as follows:

	ClF	ClF ₃	ClF ₅
$E_{\text{bond}}, \text{ eV}$	2.6	1.8	1.5

The only bond Cl—F in the ClF molecule is covalent and its energy is close to 60 kcal. One Cl—F bond in ClF₃ is also covalent and has approximately the same energy, while the other two are hypervalent bonds, and their energy is much lower. The mean energy of the two-centre bond Cl—F in the ClF₃ molecule is therefore lower than that in the ClF molecule. The picture is the same with ClF₅; the energy of each of the four hypervalent bonds is much lower than the energy of the only covalent bond (its energy being approximately the same

in the whole series $\text{ClF}—\text{ClF}_3—\text{ClF}_5$) and the mean energy of the two-centre bond $\text{Cl}—\text{F}$ is therefore the lowest in ClF_5 , which has the greatest number of hypervalent bonds.

What is important here is that in the transition from molecules having only covalent bonds $\text{A}—\text{L}$ to molecules having also hypervalent bonds, the mean energy of the two-centre interaction (the only quantity which can accurately be determined experimentally) sharply decreases and this decrease continues with the increasing number of hypervalent bonds in a molecule. Thus, the decrease in the mean energy of the $\text{A}—\text{L}$ bond in the series of compounds AL_n , at a certain value of the index n , can probably be a direct indication that molecules with hypervalent bonds appear at this given moment. This phenomenon is always observed in the transition to molecules with higher coordination numbers which follow after AF (in the 7th group), AF_2 (in the 6th group), and AF_3 (in the 5th group). In the latter case, a sharp drop of the mean energy of the two-centre bond observed during the transition from AsF_3 (5 eV), having three covalent bonds $\text{As}—\text{F}$, to the AsF_5 molecule (3.6 eV), in which two out of five $\text{As}—\text{F}$ bonds are hypervalent, is a vivid example.

It is natural that mean values of E_{bond} are quite constant in the series of molecules where hypervalent bonds do not appear; for example, the mean energies in the series $\text{PF}—\text{PF}_2—\text{PF}_3$ are 4.77, 4.77, and 5.25 eV respectively. Similarly, in the series of molecules with exclusively hypervalent bonds (fluorides of xenon, halogen fluoride anions, etc.) we should observe the same picture, viz., there should be no sharp jumps in the change of the mean value of E_{bond} . In fact, some fluorides of xenon, in which all $\text{Xe}—\text{F}$ bonds are hypervalent, have amazingly similar mean energies:

	XeF_2	$[\text{XeF}_4]$	XeF_6
$E_{\text{bond}}, \text{ eV}$	1.37	1.36	1.31

The hypervalent bond model explains Mendeleev's rule of even numbers (the rule of relatively greater energy stability of those forms of compounds of a given element of the main sub-group in which the central atom is at the stages of oxidation the even number of which corresponds to the number of the group in the Periodic system). Valency of the central atom (to be more accurate, its coordination number) cannot increase over a certain value (which is determined by the number of unpaired electrons in the valence np -orbitals of the central atom) at the expense of covalent bonds, and it increases at the expense of the formation of hypervalent bonds. But as has already been said, these bonds, with the three-centre nature inherent in them, can arise only with simultaneous attachment to the central atom of *two* new ligands, which determines the rule of even numbers

(parity rule) by Mendeleev:

7th group	ClF	ClF₂	ClF ₃		
6th group	SF	SF ₂	SF₃	SF ₄	
5th group	PF	PF ₂	PF ₃	PF₄	PF ₅

Now it has become possible to verify this rule. In accordance with the condition of the hypervalent bond model it is possible that this rule should not hold for all existing compounds of a given non-transition element, but begins to be valid only at a certain stage of oxidation of the central atom, namely, from the moment when the first hypervalent bonds arise.

It is easy to understand that this rule does not hold for chemistry of the elements in additional sub-groups where the central atoms can use all their valence ($n - 1$) d -, ns -, and np -orbitals in the covalent bonding without resorting to hypervalent bonds in their interaction with the ligands.

The theory of hypervalent bonding readily explains the phenomenon of the secondary periodicity, which is so important in chemistry of the elements in the main sub-groups. The secondary periodicity shows most vividly in the properties of the higher compounds of non-transition elements, and this important fact can be explained as follows. It has already been said that the molecules of non-transition elements incorporating the central atom at the highest stage of oxidation (corresponding to the number of the group in the Periodic system) always comprise hypervalent-2 bonds with participation of the ns^2 -valency electrons of the central atom. It is clear that the characteristics of such molecules, and first of all the total energy of bonds in them, will depend on the value of the energy of $np - ns$ separation for the valence orbitals of the central atom. It is possible to foresee that with the increase in this energy of separation, the participation of the ns^2 -valency electrons of the central atom in hypervalent bonding with ligands will be more difficult (for the energy considerations mentioned above) and this will undoubtedly decrease the total energy of bonds in molecules whose central atom is characterized by a greater difference $\varepsilon_{np} - \varepsilon_{ns}$. Below given are mean energies of the two-centre A—F bonds for hexafluorides of non-transition elements of the 6th group and the energies of $np - ns$ separation, characteristic of their central atom [12, 13]:

	OF ₂	SF ₆	SeF ₆	TeF ₆	PoF ₆
$E_{\text{bond}}, \text{ eV}$	none	3.16	2.97	3.42	(2.47)
	O	S	Se	Te	Po
$\varepsilon_{np} - \varepsilon_{ns}, \text{ eV}$	14.9	9.8	10.4	8.8	(12)

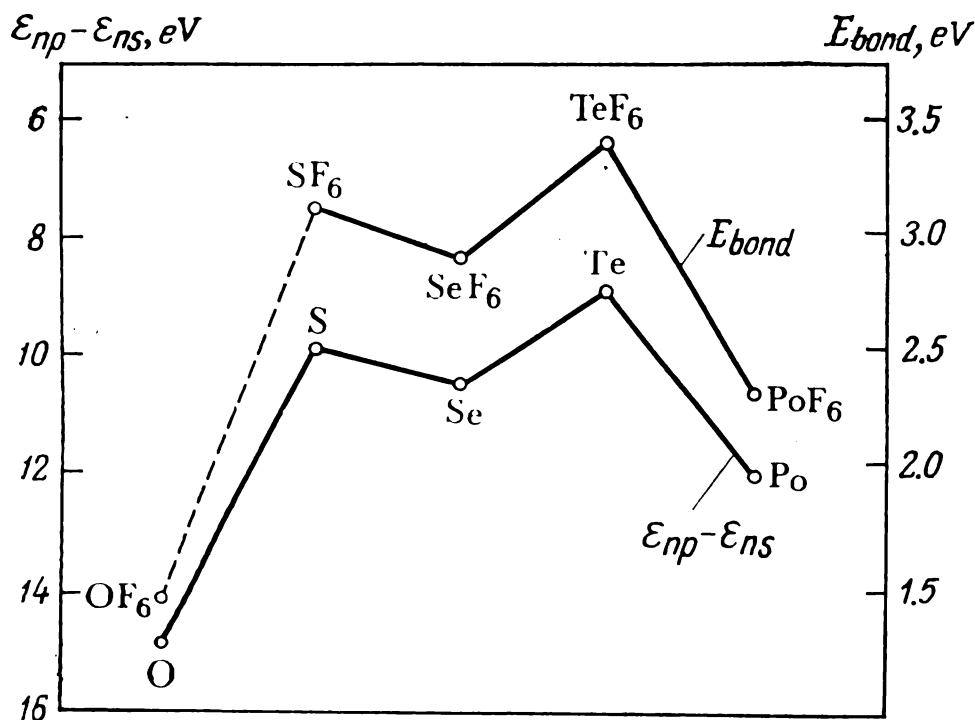
It is quite obvious (see also Fig. 4) that the secondary periodical dependence of E_{bond} precisely reflects the secondary periodical dependence of the separation energies of the np - and ns -valence orbitals of the central atoms.

It is easy to understand that the difference in the orbital energies of the valency np - and ns -electrons is not very important for the energy characteristics of compounds with decreased formal valency of the central atom, in which there are no hypervalent-2 bonds between the central atom and the ligand requiring the participation of its valency ns^2 -electrons, but there are hypervalent-1 and covalent A—L bonds. Therefore the secondary periodicity markedly diminishes in series of such compounds and is only retained as a result of non-monotonous change in energies of the valence np -orbitals of free atoms in the main sub-group. The more so the secondary periodicity is close to degeneration in the energy characteristics of molecules with low formal valency of the central atom where hypervalent-1 bonds are not found either, and there are only ordinary covalent A—L bonds.

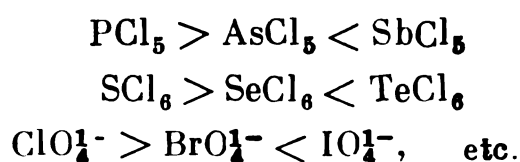
Thus, the secondary periodicity can actually be revealed only with the appearance of hypervalent bonds in molecules.

Given below are the energies of separation of the np - and ns -valence orbitals of the atoms of non-transition elements standing in the 3-8th groups [13]. The data indicate that for the atoms of the elements belonging to the fourth period (Ga, Ge, As, Se, Br) this difference is always higher than for the atoms of the elements of both the

Fig. 4. Mean energies of two-centre A—F bonds in molecules of hexafluorides of chalcogenides and energies of np — ns separation for free atoms of oxygen, sulphur, selenium, tellurium, and polonium.



third (Al, Si, P, S, Cl) and the fifth (In, Sn, Sb, Te, I) periods. This specificity of the atoms of the elements standing in the fourth period [14] is probably very important for the determination of relative stability of their higher compounds. Thus, hypervalent compounds of non-transition elements of the 5-7th groups (As, Se, Br) are characterized by lower stability of their higher compounds compared with those of the elements standing on their either side in the group:



Thus, with the increasing energy of np — ns separation, the role of the ns^2 -valency electrons of the central atom ($4s^2$ -electrons of the atoms of the elements standing in the fourth period) in bonding with ligands decreases. This in turn decreases the total energy of bonds in those molecules where the central atom always forms hypervalent-2 bonds with its ligands, i.e. shows its maximum valency. After all, it decreases the energy stability of the higher compounds of those non-transition elements whose atoms are characterized by the maximum energy difference.

When viewed from the same standpoint, it is easy to understand the abnormal energy characteristics of the higher compounds of non-transition elements of the sixth period (Tl, Pb, Bi, Po, At, Rn), for whose atoms the energy of np — ns separation is very high. The great differences in the orbital energies of the $6s$ - and $6p$ -valency electrons in the atoms of these elements account for the so-called "inert pair effect" and sharply decrease the energy stability of the higher oxidized forms of the elements closing the main sub-groups (Table 16).

This tendency is fully absent in chemistry of the transition metals. On the contrary, the stability of higher oxides steadily increases in

Table 16. Energies of ns — np Separation in Atoms of Non-transition Elements

Period II	B	C	N	O	F
	4.6	5.3	6.0	14.9	20.4
Period III	Al	Si	P	S	Cl
	4.5	5.2	5.6	9.8	11.6
Period IV	Ga	Ge	As	Se	Br
	5.9	6.4	6.8	10.4	12.0
Period V	In	Sn	Sb	Te	I
	5.2	5.8	6.6	8.8	10.1
Period VI	Tl	Pb	Bi	Po	At
	(7)	(9)	(10)	(12)	(16)

the additional sub-groups as we pass over to metals of the sixth period ($\text{CrF}_6 \ll \text{MoF}_6 < \text{WF}_6$). The decreasing stability (sometimes to complete instability) in the higher compounds of the $3d$ -elements is probably connected with the abnormally high energies of vacant $4p$ -orbitals of these atoms, without which the high coordination of the central atom is impossible. The participation of the vacant $4p$ -orbitals in the bonds with ligands during hybridization of all valence $sp^m d^n$ -orbitals of the atom of a transition metal is hindered by their energetical "remotedness" from the other valence $3d$ - and $4s$ -orbitals.

It is also important to note that the hypervalent bond concept explains the absence of higher compounds in the elements of the second half of the Period II (N, O, F). The absence of NF_5 , OF_6 , and so on, should be associated with the great (the greatest for the atoms of the elements of this main sub-group) difference in the orbital energies of $2s$ - and $2p$ -valency electrons of the atoms of these elements and with complete inability of the $2s^2$ -electrons to participate in the formation of hypervalent-2 bonds with the ligands (fluorine atoms), without which the higher compounds cannot be formed. It is also possible to explain instability of oxygen tetrafluoride, OF_4 . BF_4^{1-} , CF_4 , and NF_4^{1+} are stable because all these molecules incorporate four ordinary covalent bonds $\text{A}-\text{F}$. Unlike these molecules, the OF_4 molecule could have been formed on the condition that two $\text{O}-\text{F}$ bonds were hypervalent-1 bonds. But the energy of such three-centre four-electron interaction (at the expense of the $2p$ -electron pair of the oxygen atom and one unpaired $2p$ -electron of each of the two fluorine atoms) could have been sufficient to form a stable bond only on the condition that the electronegativity of the central atom should be small, so that the valency electron charge of the central atom could be re-distributed between the ligands. This condition is not fulfilled in oxygen fluorides. The re-distribution of the valency electron density onto the ligands (in the formation of hypervalent bonds) is practically impossible if an oxygen atom, characterized by very high electronegativity, acts as the central atom. It is therefore hardly possible in general that hypervalent bonds could be formed in molecular systems of oxygen fluorides. Hence, it is also hardly possible that oxygen fluorides higher than OF_2 , with ordinary covalent bonds, could be formed.

Such examples are not numerous, but they concern important problems of inorganic chemistry of the elements of the main sub-groups, and indicate that the hypervalent bond theory can successfully be used to explain many interesting regularities connected with the Periodic system and valency [15, 16, 17].

The idea of orbital-deficient molecules with three-centre four-electron hypervalent bonds seems to be more fundamental than the traditional idea of covalent bonding between the central atom and

the ligands. Unlike the former ideas of hybridization of valence orbitals of the central atom, the theory of hypervalent bonds in molecules of the elements standing in the main sub-groups fully corresponds to both experimentally found and theoretically calculated characteristics of the electron structure of these molecules; this theory is general in its essence and can give a simple explanation to many (if not all) aspects of the chemistry of coordination compounds of non-transition elements. Using the same approach, namely the concept of hypervalent bonds arising from the three-centre four-electron interaction makes it possible to describe the nature of the compounds of noble gases, molecules of interhalogens and their anions, higher compounds of the elements standing in the main 5-8th sub-groups, their sandwich compounds [8], the hydrogen bond which, in this theory, looks like an ordinary coordination bond formed by the atoms of non-transition elements (the unbreakable linearity of the three-atom fragment $X-H-Y$ is also explained), and also probably cluster groupings incorporating atoms of the heaviest non-transition elements Tl, Pb, Bi, etc. It can be shown that the hypervalent bond theory can explain molecular structures of boron hydrides; the only point which requires special consideration is that the bond in the fragment $B-H-B$ is a three-centre two-electron hypervalent bond and boron hydrides should therefore be classified as orbital-excessive or electron-deficient molecules. The angular structure C_{2v} of the fragment $B-H-B$ is in this situation *always* advantageous from the energy point of view because only the lowermost (with respect to energy) bonding molecular orbital φ_1 is filled here with two electrons; and vacant now is not only the antibonding φ_3 but also non-bonding φ_2 molecular orbital (in contrast to the three-centre four-electron bonds). In fact, in absolutely all molecules of boranes, the grouping $B-H-B$ is always bent.

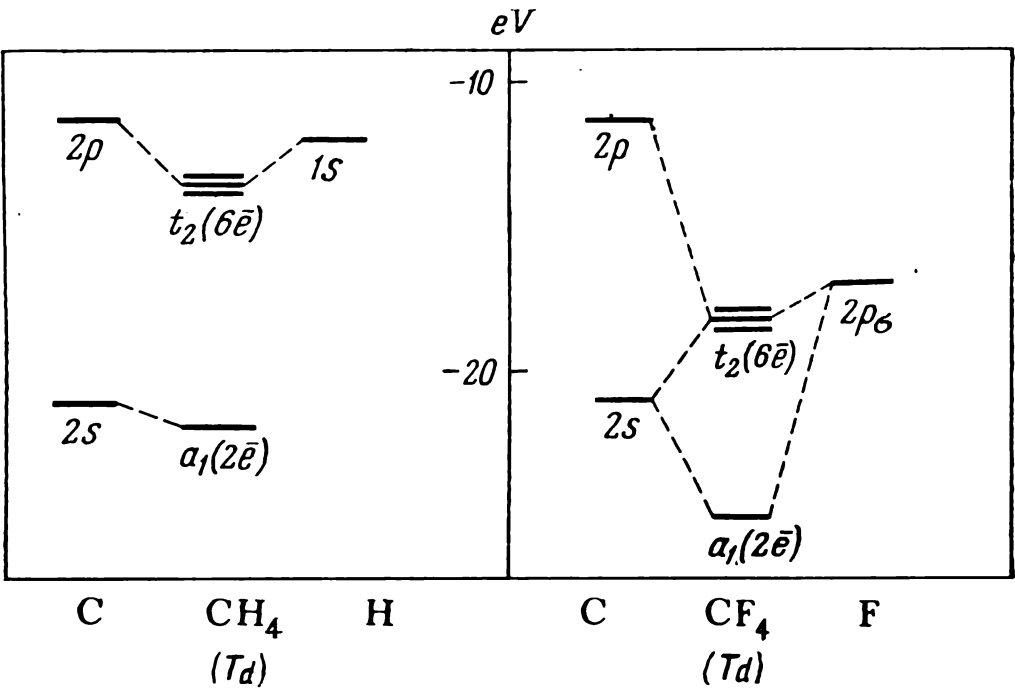
From the point of view of the theory of hypervalent bonds in molecules of non-transition elements, the ordinary idea of hybridization of valence atomic orbitals can probably be extended to the molecules whose central atoms have the coordination number ≤ 4 . And here we can only speak about hybridization of the sp^m -type and only for non-transition elements of the first half of the period (for BH_4^{1-} , BF_4^{1-} , CH_4 , CF_4 but not for SF_4 , IF_4^{1-} , XeF_4). But unexpected phenomena can be encountered even in cases that seem quite simple at first sight. The molecule of methane, strange as it may seem to the reader, stands in the first rank of such unexpectedness. The situation with hybridization of the sp^3 -type is not at all simple with this molecule. Since the $2s$ -orbital of the carbon atom is much lower (with respect to energy) than the $1s$ -orbitals of the hydrogen atoms (Fig. 5), two electrons $2s$ (C) in the CH_4 molecule form a substantially unshared electron pair (both molecular orbitals of the a_1 symmetry remain substantially non-bonding). This indicates that the C—H

bonds in the CH_4 molecule arise mainly at the expense of the $2p(\text{C})-1s(\text{H})$ interaction owing to the population with six electrons of triply degenerate bonding molecular orbital having the symmetry t_2 . The $\text{C}-\text{H}$ bonds in CH_4 are therefore orbital-deficient hypervalent-2 bonds rather than ordinary bonds, and the observed tetrahedral geometry of the CH_4 molecule is not at all connected with the sp^3 -hybridization, but remains dependent on the minimum energy of the interligand repulsion for the tetrahedral configuration of the molecule formed by the interaction of σ -orbitals of four equivalent ligands (hydrogen atoms) with three Cartesian valence σ -orbitals of the central atom (carbon atom).

The picture is quite different with the electron structure of the CF_4 molecule. The energy of the $2p_\sigma$ -orbitals of the fluorine atoms is much closer to the energy of the $2s$ -orbitals of the carbon atoms (Fig. 5) than the energy of the $1s(\text{H})$ to that of $2s(\text{C})$ orbitals. Therefore even $2s^2$ -valency electrons of the carbon atom in the CF_4 molecule take part in bonding with the ligands (the molecular orbital a_1 is also strongly bonding), and the molecule CF_4 comprises four covalent bonds $\text{C}-\text{F}$ formed by eight (not by six as is the case with CH_4) bonding electrons. A very simple fact convincingly proves that the structures of the CH_4 and CF_4 molecules are strikingly different: in *all cases* of transition from hydride to fluoride, in molecules where the central atom is O, N or F, the mean energy (eV) of the two-centre bond $\text{A}-\text{L}$ markedly, and sometimes very sharply, drops:

CH_4	4.3	NH_3	4.07	OH_2	4.79	FH	5.9
CF_4	5.1	NF_3	2.9	OF_2	2.17	FF	1.6

Fig. 5. Energies of occupied molecular orbitals in CH_4 and CF_4 molecules.



All these hydrides and fluorides of nitrogen, oxygen, and fluorine have exclusively ordinary covalent bonds. The exception is the case with carbon: E_{bond} increases in the transition from CH_4 to CF_4 . This can easily be explained if we remember that the hypervalent molecular structure of CH_4 is converted here into the structure of CF_4 characterized by exclusively covalent bonds, which are stronger from the energy point of view.

So, practically all compounds of non-transition elements, which have more than four ligands, are coordination compounds in the sense that all their σ -bonds $\text{A}-\text{L}$ cannot be ordinary two-centre two-electron bonds (with the $sp^m d^n$ -hybridization of valence orbitals of the central atom). The concepts of the $sp^m d^n$ -hybridization can only be used to describe bonds in compounds of the transition metals, where the use of these concepts is justified by the valent basis of the central atom itself, which comprises the orbitals of all types (s , p , d). Such an extension of the valent basis to the atoms of the transition metals results in a quite different stereochemistry of their complexes (compared with that of coordination compounds of non-transition elements; cf. MoF_4 and SF_4); they are characterized by the formation of multiple bonds $\text{M}-\text{L}$ in contrast to the predominantly ordinary σ -bonds $\text{A}-\text{L}$ in complexes of non-transition elements characterized by coordination numbers greater than 4.

References

1. Coulson, C. A., *Valence*, Oxford, 1961.
2. Gillespie, R. J., *J. Chem. Educ.*, 1970, v. 47, p. 18-22.
3. Dyatkina, M. E., *ZhVKhO im. Mendeleeva*, 1972, vol. 17, No. 3, p. 285-292.
4. Johnson, K. H., *Adv. Quant. Chem.*, 1973, v. 7, p. 143-185.
5. Musher, J. I., *J. Amer. Chem. Soc.*, 1974, v. 94, p. 1370-1371.
6. Nakatsuji, H., Musher, J. I., *Chem. Phys. Lett.*, 1974, v. 24, No. 1, p. 77-80.
7. Musher, J. I., *Angev. Chem. Intern. Edit.*, 1969, Bd. 8, S. 54-70.
8. Musher, J. I., *Tetrahedron*, 1974, v. 30, No. 13, p. 1747-1751.
9. Koutecky, V. B., Musher, J. I., *Theor. Chim. Acta*, 1974, v. 33, No. 3, p. 227-238.
10. Pimental, G. C., Spratley, R. D., *Chemical Bonding Clarified Through Quantum Mechanics*, San-Francisco, Cambridge, London, Amsterdam, 1970.
11. Linnet, J. W., *Valency and Mendeleev's System*, in the book "Centenary of the Periodic Law of Chemical Elements", Nauka, 1971, p. 103-112 (in Russian).
12. Moore, C. E., *Atomic Energy Levels*, Washington, 1958.
13. *Molecular Structure and Quantum Chemistry*, "Naukova Dumka", Kiev, 1970, p. 155-175 (in Ukrainian).
14. Nefedov, V. I., *Zhurnal strukturnoi khimii*, 1974, v. 15, No. 6, p. 1093-1098 (in Russian).

15. Syrkin, Ya. K., Periodic System and Valency Problems, in the book "Centenary of the Periodic Law of Chemical Elements", Nauka, 1971, p. 85-102 (in Russian).
16. Syrkin, Ya. K., Periodic System and Valency Problem, Znanie, 1971 (in Russian).
17. Shchukarev, S. A., *Modern Importance of Periodic Law of Mendeleev and Prospects for Development*, in the book "Centenary of the Periodic Law of Chemical Elements", Nauka, 1971, p. 40-53 (in Russian).

The Results of the Historico-logical Analysis of the Valency Problem

We have, in the general outlines, reconstituted the history of the theory of valency. This has given us a wealth of material about the sources from which the valency concept arose, the evolution of this concept, its role in the development of theoretical chemistry, and, finally, explained the causes of the difficulties which arose with the extension of the valency concept to various objects of chemistry. This material enables us to draw the conclusion about the tendencies in the development of the theory of valency, and about the history of the concept itself.

1. General Tendencies in the Development of the Theory of Valency

Chapters 2 through 6 describe the development of the valency concepts. The picture is very complicated. It appeared to be even more complicated than the evolution of the concept of the chemical element, for which valency is only one of the attributes. The complexity however is explained by the factual material of the history of the valency theory itself. And the main point here is not only the divergence of the valency concept, on which we dwelt so much in this book, but the fact that the valency concept is brought to those extreme limits where it turns to be everything or nothing.

In fact, the valency concept which first appeared in the 1850s to give quantitative characteristics of chemical affinity of atoms, in the 1860s was already used as something equivalent to the chemical bond. In the works by Frankland (1866-1868) the concepts of atomicity and bond were formally identified. Kekulé identified the unit of atomicity with the unit of bond. Couper and Crum Brown were the first to show the chemical bond as the interaction of two affinity units and designated it by valency dashes. And at this stage, only one step was left to the identification of the term "chemical interaction" with "valence interaction". And this step was made.

One might think that this could only add to credit of the valency

concept. But in fact it appeared to be the source of danger. The continuous widening of the valency concept against the background of its indefiniteness (valency was regarded as a unit of affinity of a free atom, as a characteristic of a bound atom, as a partial or residual valency, etc.) gradually resulted in the identification of this concept with chemism in general. The books by Murrell, Kettle, Tedder [1] and Coulson [2] convincingly prove it. These books are dedicated to valency and yet they do not describe valency. According to these authors valency is everything and nothing; they regard it as the entire chemism without attributing any concrete meaning to the term "valency" which they put in the title of their books.

It is quite clear that with this approach, the concept of valency becomes useless. The theory of valency itself becomes senseless; it transforms into a theory of valency as a *universum* of the quantum-chemical methods.

But this is only one of the tendencies in the development of the valency theory, namely the tendency which leads to a complete collapse of the theory itself. Its motif is the logically irrational widening of the important, but strictly specific chemical category, the valency concept, its extension to various chemical objects which have no systemic connections between each other. Here we meet with the volitional subversion of a concept through a logically unlawful exaggeration of its meaning, which becomes the cause of deviation of history from logics.

But logics in our case prohibits the collapse of the valency theory, and it will survive because any theory, whose validity is proved by experience, cannot be shifted aside as something false; it retains its importance in its field, and is included into new theories as a limit form or a special case [3]. The theory of valency, which has become inseparable from practical and theoretical chemistry, cannot be rejected altogether, and more general theories have appeared. Like the classical theory of chemical structure, which arose from the valency theory, the latter, with the extension of the laws of physics to chemical phenomena, will, as Butlerov put it, "... be overthrown like the old chemical theories were overthrown; but, like most of these theories..., it will not... disappear completely, but, in the changed form, it will be included into new, wider conceptions" [4, p. 383].

Chapters 2 to 6 show that along with this tendency there are some other, and much more important tendencies in the development of the theory of valency. In one of them valency is considered as a reactive power of an isolated atom. Another tendency is to regard valency as the structural characteristics of the atom bound in a molecule, i.e. of an element in stabilized orderly system.

These tendencies are so important that we must dwell on them in more detail.

2. Valency as a Reactive Power of an Isolated Atom

In the discussion of the complex situation of the modern state of the valency problem (Chapter 1) we have separated a question the answers to which have become the first cause of the divergence of the valency concept. The question is whether valency is the property of an isolated or a bound atom. And we cited, in the same chapter, Tatevskii [5] who wrote in 1965 that "in the classical theory of chemical structure", the valency concept was used to characterize the state of an atom bound in a molecule, but not in the free, or unlinked state. As far as an isolated atom is concerned, "this question, according to Tatevskii, was senseless in the classical theory of chemical structure", because "valency of a free atom in classical theory is zero" [5, p. 37-38]. A less resolute statement can be found in another work by Tatevskii [6, p. 49, 156].

Now, as we got acquainted with the history of the creation of the valency concept and the development of ideas incorporated in this concept in classical chemistry (see Ch. 2 and 3) we know that Tatevskii was wrong. It is in the classical theory of chemical structure that valency is regarded exclusively as the property of an isolated atom, as its potential power to form compounds. And this is very important for the study of the evolution of the valency concept and, after all, for the prediction of the future of this concept.

[Valency as a force causing "chemical phenomena" in classical chemistry. Chapter 2 shows, firstly, that the valency concept arose from pre-Butlerov theories, from the study of the action of stoichiometric laws during the formation of particles of chemical compounds, and secondly, from the study of the structure, or constitution, of these particles. In Frankland's works this concept was coordinated with the law of equivalents and was called the "combining power". In Kekulé's works it had to perform the role of a clue to the study of the modes of attachment of atoms to one another during the formation of a molecule. "I suggest, wrote Kekulé, that the nature of both radicals and their compounds be derived from the nature of the elements. My earlier ideas of the nature of elements and basicity of atoms can serve as the starting point" [7, p. 14]. By basicity of atoms Kekulé understood the number of affinities which are inherent in the atom of any given elements when it is combined into a molecule. "As the atoms touch each other, each affinity unit of a given atom combines with an affinity of another atom" [7, p. 25]. And here Kekulé states that the affinities of an atom can be used either completely or only partially. For example, he supposed that SO_2 is a radical consisting of three atoms, each of which is "diatomic". Hence, "of the six affinities, four ... are used to hold three atoms together, while two

affinities remain unused" [7, p. 25]. These two free affinities make SO_2 a free radical, sulphuryl, capable of attaching two "monatomic" atoms of chlorine and give "chlorosulphuric acid" (sulphuryl chloride).

The valency theory by Kekulé was the foundation, or the main precursor, for Butlerov in the creation of his theory of chemical structure [4, p. 68]. But Butlerov, as he developed the idea of formation of compounds from "elementary shares", i.e. from atoms, used the term atomicity to describe the properties of a free atom, or to describe the quantity of free affinities: "Each elementary share has a pre-existing amount of force which produces chemical phenomena (affinities). As a chemical compound is formed, part ... of this force or its whole amount is consumed" [4, p. 71]. Butlerov resolutely rejected the idea that valency is the characteristic of an atom bound in a molecule and that it does not mean anything when applied to isolated atoms. There is the following statement among his eight rules "how to determine the chemical structure": "An atom having two units of free affinity can exist independently, i.e. can form a particle" [4, p. 72].

We returned to the facts with the intention to clear out with certainty what was meant by valency in the theory of chemical structure, the basis of classical chemistry.

So, first valency was regarded as the quantitative (measured in whole numbers) characteristic of free affinity inherent in an isolated atom of a given chemical element. These were, in fact, the first fundamental concepts of reactivity of atoms, which united in themselves all advances in the science of chemical atoms and the first structural theories, the Butlerov theory of chemical structure included.

Chapter 3 shows that the discovery of the periodic law and intense investigations in the field of periodicity gave a new stimulus to a sort of emancipation of the theory of valency. This theory, which had been evoked by the demands of the developing structural ideas and had first been nursed by the theory of structure, was now filled with new contents with the discovery of the periodic law. First of all, the connection between the element position in Mendeleev's system and the "highest" valency of this element was established. The highest valency was understood by chemists as the number of free affinities of an atom, which expresses its reactivity, and the latter therefore appeared to be directly determined by the number of the group of the Periodic system. Next Mendeleev showed that the sum of the highest valencies of an element which it displays in its oxygen n_{O} and hydrogen n_{H} compounds is always eight: $n_{\text{O}} + n_{\text{H}} = 8$. The number of eight was coordinated with the number of groups in the table of elements, which was another indication of the deep regularities which connect valency with the nature of the element.

Chapter 6 shows that the new contents of the valency concept became one of the main fragments in the theory of periodicity. This fragment was independent and integral, including all information from organic and inorganic chemistry. In the relationships with the classical theory of periodicity, the concept of valency still remained the reflection of *valency potentialities* of atoms, although the desire to see in valency "basic properties", i.e. certain invariant characteristics of an element, led to syncretization of this concept: chemists wanted to see in valency the combination of various characteristic properties of both free and bound atom. And such a reconciled combination of two different concepts within one concept did not, at that time, hamper the study of the regular variations in the properties of elements depending with their position in the series and groups of the Periodic system; on the contrary in many respects it facilitated these studies. This appeared as a result of integration within one concept of much data concerning the valency potentialities of atoms and realization of these potentialities as examined on the simplest compounds—oxides, some few hydrides, and halides.

It was with the creation of the Periodic Law that there appeared the first ideas concerning the genetic regularities of variations in the valency of elements in the vertical and crosswise direction in the periodic table. What puzzled the investigators as they examined the crosswise valency variations was the invariable number of *eight*, while the effect of the atomic mass on the character of display of valency (i.e. on the degree of utilization of free affinities) was quite vivid in the vertical direction. But they did not establish, in accordance with the classical theory of periodicity, the nature of valency; nor did they discover the cause of periodicity itself either.

This was done only by the electron theory.

Valency as spin-valency. Ways to understanding valency in the sense as it is understood in the quantum-mechanical VB method were marked before the emergence of the electronic theories in chemistry. Delavaud's hypothesis (see Chapter 2), some mathematical analogies of Sylvester, Clifford, Gordon, and Alexeyev (Chapter 5) were the first landmarks in this way. One may dispute the importance of these purely phenomenological or purely formal hypotheses for the development of the spin-valency theory; this is not essential. What is essential is that *these hypotheses emerged one after another, they did exist, and thus indicated the general tendency in the development of the concept of valency as reactivity of free atoms.*

Chapter 5 shows how this tendency developed. The very first electronic theories disclosed the physical sense of the character of valency which is expressed in whole numbers, explained the mystery of the number of eight. Despite the significant difference between these theories, they all were unanimous about one conclusion: to each single valency as a unit of free affinity there corresponds one

electron in the outer shell of an unlinked atom. Although these theories, based on the ideas of classical electrodynamics, could not explain the causes of pairing of electrons with like charges (which must repel one another), they gave answers to many other questions which had long been the source of trouble for the chemists. These theories described in detail the valency potentialities of the atom, proceeding from the first models of the electron structure of atoms and from the wealth of empirical data.

The quantum-chemical valence bond method is actually a logical synthesis of the postulates of the electronic theories by Lewis and Langmuir on the one hand, and of the wealth of material of classical chemistry* on the other hand, as well as on an entirely new foundation, *viz.*, quantum mechanics.

We have already said in Chapter 5 that valency in the VB method is a number of unpaired electrons in the outer electron layer of a free atom. The VB method postulates that a shared electron pair, or a chemical bond between two atoms, can be formed on the condition of anti-parallel spins of unpaired electrons. Hence the special term *spin-valency*.

The combination of postulates describing the spin-valency concept, the methods of determining its number and the function of this concept in chemistry is the theory of spin-valency [9]. This theory is based on the periodic law of chemical elements and on the valence bond method.

The spin-valency theory draws the information on the structure of the outer electron layers of atoms, and hence on the quantity and the energy state of unpaired valency electrons, from the theory of periodicity, and from the quantum theory of the Periodic system in particular [10, 11]. When the spin-valency theory derives valency numbers and chemical activity of elements from the Periodic system, it functions mainly as a deductive theory. In this case it takes characteristics of the valency potentialities of the atoms from the periodic theory of the atomic structure.

This way of obtaining information on the valency potentialities of atoms is, in principle, the most rational one, i.e. the most convenient, because it takes various information from one source. This is why it is useful... but its use is only limited. The valency potentialities of an atom, like all possibilities in general, are not reality. The potentialities turn into reality only by the interaction between at least two atoms, and new factors therefore appear which stimulate additional reactive possibilities of atoms.

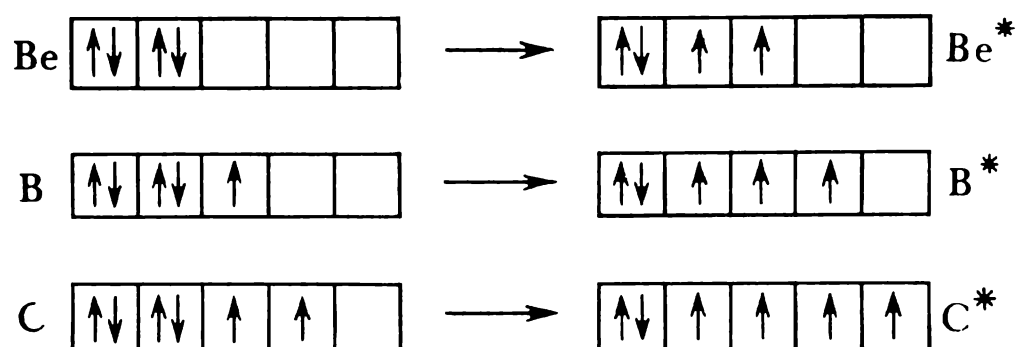
The spin-valency theory, in addition to the Periodic system, also uses the VB method for theoretical processing of the material concern-

* This comprises not only the vast experimental data but also theories, e.g. the theory of Werner, which Lewis chose for himself as the starting point.

ing the existing chemical bonds. From the VB method it takes the information on the methods and mechanisms of realization of valency potentialities, i.e. it derives the information on the causes of chemical aggregation of atoms from the effects. Here it functions not only as a deductive theory but also as an inductive one, verifying it and, as a rule, adding to its deductive conclusions.

The illustration of its deductive and inductive functions is the determination of the valency number of the elements of the first and second periods [12]. In accordance with the Periodic system of elements, spin-valency is derived here from the structure of the electron shells of the atoms (Table 17).

Spin-valency determined for seven elements by the deductive method does coincide with the actually observed valency of these elements, but for three elements, viz., beryllium, boron, and carbon, this coincidence is absent: the experimentally found valencies of these atoms are 2, 3 and 4 and not 0, 1, and 2, respectively. The spin-valency theory, referring to the valence bond method, explains this incongruity by the transition of the atoms from the ground state to the *excited*, or *valent*, state:



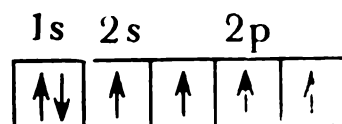
This transition consumes energy which, as the literature indicates [12-15], is compensated for in excess by the formation of additional chemical bonds.

We are not going to expound the theory of spin-valency here. It has been well described in textbooks. But in order to establish the general tendencies in the development of the valency concept we must pay special attention to the correlation between the concepts of *spin-valency* and the *valent state*.

Spin-valency, according to all definitions, is the reflection of the valency possibilities or chemical potentialities of a free atom. But what is the valent state? Is it a state of a free or a bound atom? To find the answer to this question is as important as to answer the question what valency itself actually is: whether it is the property of an isolated atom or of an atom bound in a molecule?

The literature does not give any objective criteria for the valent state concept, while there are quite different opinions as to what this concept characterizes.

Volkenshtein, for example, believes that the excited state of a carbon atom is the "true valent state" and suggests that it is described as follows [12]:



The "Course in Chemistry" [14] intended for higher school discloses this subject in the same way. Spin-valency is defined in this textbook as a "number of unpaired electrons of an atom in the excited state" [14, p. 101]. According to some other authors, the "valent state ... is hypothetical"; this opinion probably derives from the fact that the valent state has not been established as a real physical phenomenon by any of the existing methods. Coulson also indicates that there are some discrepancies connected with this problem:

- (1) this state cannot be observed spectroscopically;
- (2) the carbon atom in methane never passes into the valent state [2].

But since the valent state concept has long been included into theoretical chemistry and is a suitable method to explain the real valency potentialities of an atom, it is desirable that these discrepancies should be removed. And there is a straight logical way to do it.

Table 17. Spin-valency of the Elements of the First and Second Periods of the Periodic System

Element	Electron structure	Spin-valency
	$ \begin{array}{ccccc} 1s & 2s & & 2p & \\ \boxed{\uparrow} & & & \boxed{} & \boxed{} \end{array} $	
1. H	$\boxed{\uparrow}$ -----	1
2. He	$\boxed{\uparrow\downarrow}$ -----	0
3. Li	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ -----	1
4. Be	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ -----	0
5. B	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ -----	1
6. C	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ -----	2
7. N	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ -----	3
8. O	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ $\boxed{\uparrow}$ -----	2
9. F	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ -----	1
10. Ne	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ -----	0

First of all, proceeding from the trivial requirements of logics, viz., not to confuse the cause and the effect, it is impossible to interpret the valent state concept as a state of an atom in a molecule. The VB method considers the chemical bond in a molecule as an electron pair common for two nuclei, and explains spin-valency of an isolated atom as a number of still unpaired electrons, corresponding to the number of valence bonds formed by this atom with the other atoms. The spin-valency concept arises in the VB method first of all in order to explain the *mechanism of formation of a chemical bond*. Spin-valency of carbon, which is equal to four, is necessary to the VB method for the same purpose, irrespective of the fact whether the formation of methane is a single-step ($\text{C} + 4\text{H} \rightarrow \text{CH}_4$) or a two-step ($\text{C} + 2\text{H} \rightarrow \text{CH}_2$; $\text{CH}_2 + 2\text{H} \rightarrow \text{CH}_4$) process. Hence, the VB method does not identify the cause (spin-valency) with the effect (chemical bond, or valency potentialities and actual valence bonds) but only demands their numerical congruence. Therefore the VB method uses the valent state concept only to compensate for the deficiency of the valency number, which is determined from the electron configuration of the atom in the ground state, to bring it to the valency number which must satisfy the principle of equality of the number of unpaired electrons of an isolated atom and the electron pairs surrounding this atom in a molecule.

Secondly, it is important to emphasize that the valent state concept is useful because of its models of the *transition* of the $2s$ -electron onto the $2p$ -sub-level. According to these models, such a transition gives a system having a maximum of unpaired electrons ready to form bonds. It is this pre-reaction system that explains the mechanism of chemical aggregation of atoms into a molecule. Therefore, and also because a saturated molecule does not contain unpaired electrons, the advantages of the models employed in the valent state concept completely disappear as the models are extended to a formed molecule.

Thirdly, the valent state is, according to some authors, a "hypothetic state". And they think it is so not only because this state cannot be confirmed spectroscopically, but also because it is an idealized model of a certain transition state of an atom whose outer electrons start re-arranging under the effect of a virtual energy gain. The hypothetic and ideal character, which is ascribed here to this concept, is not more hypothetic or ideal than that of the concept of an isolated atom. Neither Kekulé nor Butlerov ever isolated (and were not going to isolate) a carbon atom in the free state. But this did not stop them from making conjectures concerning the atoms in the free state and their free affinities. Such conjectures are the starting abstraction from which the concrete arises. Butlerov started from abstraction to understand deeper the role of the structure in the genesis of the properties of molecules; the VB method went

through abstraction to the study of the mechanism of bond formation, to the study of atomic orbital hybridization and spatial directionality of valence bonds in particular. As to Coulson's statement that valent state is not spectroscopically proved, that when scientists speak about excitation of an atom into the valent state, they do not describe the actual or at least physically feasible process, we must admit that this statement is untenable. If there exists and functions in science a certain idealization, for example, resonance of structures in the theory of resonance, or the valent state in the VB method, there are no grounds for the assertion that this is only a convenient fiction: the reverse of any idealization, as a method of reflection, is objectivization. And if the valent state is only hypothetic today, tomorrow it can become an empirical reality.

This discourse was necessary to clear out the concept of spin-valency and also to show the logical unlawfulness of applying the valent state concept to the atom bound in a molecule.

The ideas of spin-valency are very important in the general tendency of development of the concept of potential possibilities of a free atom, i.e. its ability of chemical action. These concepts

(1) have disclosed the physical sense of the classical concept of the affinity unit;

(2) have created a quantum-chemical equivalent of the Kekulé-Butlerov valency concept, expressed by the whole number of free affinities;

(3) have established, for hydrogen, carbon, oxygen, and some other elements and their organic compounds, the cause of numerical equality of the valency of a free atom ("the number of free affinities", or spin-valency) and the valency of an atom in a molecule (the number of valence bonds or shared electron pairs surrounding the atom);

(4) have confirmed Butlerov's idea of the cause-and-effect relationships between the valency of free atoms and the chemical bond.

For more details on the fruitful use of the spin-valency concepts in chemistry, see Refs. [2, 9, 12, 13, 15-17].

Reactive power of atoms. Despite what has been said, we have to state that the spin-valency concepts are limited in their significance when applied to the mentioned trend in the development of the ideas of potentialities of free atoms. They are only important for chemistry of classical, predominantly organic molecules. The theory of spin-valency cannot explain the reactive possibilities of atoms in those numerous cases where the atoms form non-classical molecules, such as, for example, ferrocene, dibenzenechromium and other sandwich compounds, compounds of noble gases XeF_2 , XeF_4 , and also compounds of the $\text{C}_{10}\text{H}_{10}$ type. It does not show what properties of atoms are responsible for the creation of a multitude of various complex compounds. This theory can (only in rare cases) explain the valency

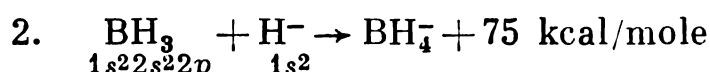
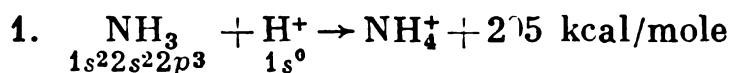
potentialities of atoms during the formation of crystals, and cannot explain the formation of surface compounds.

In all these cases (and their number can be not less than the number of cases of the formation of organic and the simplest inorganic molecules) the reactive power of atoms is determined not only by the number of unpaired electrons, but by some other factors (see Chapters 6 and 10). These factors are established by two ways:

(1) by the analysis of the existing chemical bond, i.e. by studying the causes on the basis of the information on the effects;

(2) from the knowledge of the electron configuration of the atom shells, i.e. by deductive derivation of the structure and properties of molecules from the atomic structure.

The concepts of the donor-acceptor bond and its factors (the presence of an unshared pair electrons in the donating atom and a vacant orbital in the accepting atom) thus appeared before many other concepts. More details can be found in special literature [13-16], while here we want to mention two most typical cases of the donor-acceptor interaction:

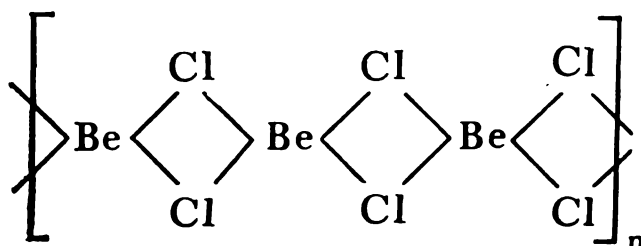


In the former case, the unshared pair of $2s^2$ electrons of the nitrogen atom passes into the molecular orbital which is their common orbital with the proton because the proton has a vacant $1s^0$ atomic orbital. In the latter case, the hydride ion H^- is the donor of the $1s^2$ electron pair, and the $2p$ -orbitals of boron in BH_3 are the acceptor.

The donor-acceptor possibilities of atoms are very great and diverse in character. And this factor significantly increases those valency potentialities of the atoms which depend only on spin-valency. In fact, all elements of the second period can, in principle, display such a donor-acceptor reactivity which increases their "classical" valency two or three times. Lithium has one $2s$ -unpaired electron and three $2p$ -vacant orbitals. Beryllium, in its valent state, has two $2s$ - and $2p$ -unpaired electrons and two $2p$ -vacant orbitals. Boron can be a kind of tetravalent because of three $2s$ -, $2p$ -, $2p$ -electrons and one $2p$ -orbital. Only carbon can be neither donor nor acceptor of electron pairs, while nitrogen, oxygen, and fluorine, in addition to their spin-valencies, can show also donating abilities, since they have one, two, and three unshared pairs of electrons respectively. Even neon can, in principle, add four donor valencies to its zero spin-valency. True, all these speculations are only based on the information concerning the structure of electron shells of atoms. The information on the existing bonds (known to chemists) introduces its corrections to moderate the actual reactive power of atoms.

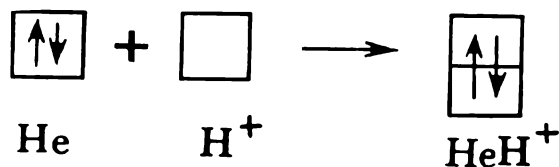
For instance, lithium, oxygen, and fluorine do not, as a rule, use all their donor-acceptor possibilities, but beryllium, boron, and nitrogen often increase their valency to four by these possibilities.

Chapter 1 gives examples of chain polymer structures of some metal chlorides. According to the classical theory of valency, and the theory of spin-valency, the formation of these compounds cannot be explained. The theory of the donor-acceptor interaction gives a quite satisfactory and trustworthy explanation. For example, beryllium



chloride forms the chain by covalent bonds Be—Cl, formed by sharing two unpaired electrons of the excited beryllium atom and two unpaired electrons of two chlorine atoms, and also at the expense of the donor-acceptor bonds formed by the donating 3*p*-electron pairs of the chlorine atoms and the accepting 2*p*-vacant orbitals of beryllium atoms. The formation of the dimer Al₂Cl₆, trimer Cu₃Cl₃, polymers of palladium chloride, etc., can be explained in the same way. The bridge structures in B₂H₆ and Al₂(CH₃)₆ are formed through the interaction of vacant orbitals of boron and aluminium with the electron pairs of B—H and Al—CH₃ bonds respectively.

The discovery of certain reactivity in the atoms of the noble gases is probably the most interesting phenomenon. Valency of the elements standing in the zero group was always assumed to be zero (from the moment of the discovery of these elements). The theory of spin-valency has explained the physical sense of zero valency: the atoms of the zero group elements have no unpaired electrons. But since they have unshared electron pairs, they are capable of giving them to the common possession with the atoms accepting these pairs. The molecular ion HeH⁺ is thus formed:



Common molecular orbitals in XeF₂, XeF₄, and XeF₆ are formed due to unpaired electrons of fluorine atoms and unshared pairs of xenon atoms. These examples explain the nature and the basic properties of fluorides of the noble gases. And now it seems strange why chemists thought it impossible that such compounds could ever exist; and when they were synthesized, early in the 1960s, they were regarded as a challenge to the theory of valency.

Still another non-spin-valency factor, characterizing the reactivity of atoms, is the factor responsible for the formation of dative bonds. These bonds are formed by unshared pairs of *d*-electrons and vacant *s*- and *p*-orbitals, which are characteristic of the transition elements in the valent state. For details see Ref. [16-18].

So, even not long ago it was possible to state that the reactivity of atoms depends on spin-valency as a number of unpaired electrons and on the donor-acceptor possibilities (dative possibilities included) which, in turn, depend on the number of vacant atomic orbitals or orbitals filled with an unshared electron pair. The reactive power of atoms could thus be characterized by whole numbers, and even now (by tradition) it is often called valency. Charkin writes in his article "Evolution of the valency and chemical bond concepts": "The extension of the theory of localized bonds to complex compounds required the inclusion of additional concepts of donor-acceptor and dative bonds ... formed by unshared pairs of one atom and vacant orbitals of the other. Our knowledge of valency of atoms has widened accordingly: bonds can be formed not only by unpaired electrons but also by unshared pairs and vacant orbitals of the valency shells. The overall valency must be equal to the number of valence atomic orbitals taking part in the bonds, since each valent atomic orbital, whatever its population may be, is potentially capable of forming one chemical bond, either Heitler-London, donor-acceptor, or dative bond" [17, p. 254].

But is the reactivity of atoms limited by these structural characteristics of the outer electron shells? Of course, not. The continuing research in this field has already given new information on the earlier unknown reactive possibilities of atoms. Chapter 10 of this book is specially dedicated to this information. The chapter describes the new theoretical conception of the electron structure of molecules of non-transition elements of the 5th-8th groups of the Periodic system, the hypervalent bonds. This new theory is undoubtedly a wider generalization of factual material, and is probably a more adequate reflection of reality. As viewed from the valency theory aspect, this new theory is also interesting in that it gives new information on the bond possibilities or, better to say, on the reactive power of atoms which shows in their interaction (in our case, in coordination of ligands round the central atom). Hypervalency is at the present time quite a new concept and it is difficult to predict how it will be (if it will ever be) expressed quantitatively. This is undoubtedly the property of atoms which results from the initiative of the partners. And this property undoubtedly resides in the various structural characteristics of the atom electron shells which, after all, are the home of all known and yet unknown reactive possibilities.

Such is the tendency in the development of our concept of valency as a reactive power of free atoms.

3. Valency as the Structural Characteristics of the Atom in a Molecule

The trend which regards valency as the property of a chemically bound atom is no less strong and important for theoretical chemistry than the trend which considers valency as a reactive power of a free atom.

Why the valency concept, which was first used to characterize a free atom, was extended to the bound atom, was explained in detail in Chapters 2 and 5. Chemists were looking for invariant properties of elements and therefore they wanted to see in valency (like in atomic mass) the main or principal properties of atoms which remain unchanged in the transition of atoms from the free into the bound state, from a simple body into a complicate one, from one compound into another compound. And as long as the number of free affinities of the atom (and later the number of its unpaired electrons) coincided with the number of simple chemical bonds formed by a given atom in a molecule, there were no doubts whether or not there is any difference between the valencies of an unlinked and a bound atom. The first doubts appeared when many cases were discovered where the number of bonds formed by a given atom did not coincide with the maximum number of affinity units. With the creation of quantum chemistry it became vivid that not only valency but even the atomic mass cannot be considered an invariant property of elements. Only the charge on the nucleus remains unchanged as an atom passes from its free state into a bound state. All other constituents of the element change to a less or greater extent. As has been noted in the previous chapter, according to quantum mechanics, atoms as such are absent in molecules: atom nuclei and electrons are the structural elements of a molecule.

But, within the allowed approximations, chemists continue speaking of "atoms" in molecules, the more so that they have certain experimental and theoretical backgrounds. But they no longer identify the valency of an atom in a molecule, a certain physical phenomenon, with the valency of a free atom, although the numerical values characterizing valency may even coincide.

How did the concept of valency of chemically bound atoms develop? The previous chapters give the following scheme by which the evolution of this concept can be traced.

The 1st stage. The valency of an atom in a molecule is determined by the number of ordinary chemical bonds formed by the given atom with other atoms. The chemical bond here is considered as a result of mutual saturation and satisfaction of free affinities inherent in isolated atoms. These concepts arose in the 1850-1860s, and actually exist now, except that they have been translated into the language

of quantum chemistry. The valency of a bound atom in the VB method means the number of shared electron pairs surrounding the atom, which are formed by unpaired electrons.

The 2nd stage. With the accumulation of knowledge of the structure of complex compounds (1870-1890), and especially with the appearance of X-ray structural data on the crystal-chemical structure of the overwhelming majority of inorganic compounds, our knowledge concerning the number of bonds formed by a given atom with other atoms in a chemical particle, has drastically changed. It turned out that these numbers are much greater than the previously determined maximum valency. This circumstance stimulated the VB method to explain the high valency numbers. The valency of an atom in a molecule was determined by this method as a total number of shared electron pairs surrounding the atom, which are formed by unpaired electrons, and unshared pairs during the donor-acceptor and dative interaction. Next, the molecular orbital method joined in to explain the high coordination numbers, and its concept of multi-centre bonds turned to be the most effective model for the purpose.

Nevertheless the classical concepts of, so to say, modest valency numbers have not disappeared. Chemists never denied that each zinc atom in zinc sulphide (ZnS) is surrounded by four sulphur atoms, and each sulphur atom is connected with four zinc atoms. But they still adhered to the opinion that the valency of zinc and sulphur in this compound is two. Despite the high coordination numbers in the oxides FeO and Fe_2O_3 , the valency of iron in the former oxide was assumed to be 2 and in the latter 3. Despite the fact that lithium atom in Li_2 has one bond, and in crystal lithium each atom is bonded with fourteen nearest atoms, the valency of lithium was considered to be equal to unity in both cases. With all interpretations of the hydrogen bond as the bridge $\text{R}\cdots\text{H}\cdots\text{R}$, chemists steadily assumed the hydrogen atom to be monovalent in the compounds with such a bond.

This stability of the tradition is explained not by the conservatism of scientific thinking, but rather by the operability of the classical concepts of valency of bound atoms, i.e. of valency which is determined by the empirical formula of composition. Suffice it to say that these valency concepts are the foundation of the successfully functioning theories of chemisorption and heterogeneous catalysis [19-21], the theory of solutions [22], and kinetics of many inorganic reactions [23].

At this second stage of development of the valency concepts, the two characteristics of a bound atom have been strictly differentiated: the coordination number, which can be determined empirically by the number of atoms surrounding a given atom and chemically bound with it, and the "valency of an element" determined from the stoichiometric formula of composition.

The 3rd stage. The classical concepts of valency of bound atoms, determined from the empirical formula of composition, differ significantly from "the number of valence bonds" developed in the VB method, and chemists therefore, in the past two or three decades, have come to another concept, viz., the concept of the *oxidation number*, or the *oxidation degree* [14, p. 238; 15, p. 149]. This concept is very close by its meaning to positive and negative valency (valencies by hydrogen and oxygen) introduced by Mendeleev. We shall not describe the essence of the oxidation number concept and the method of its determination: this has been done in textbooks [14]. This concept is very convenient for teaching, because it makes possible to pass from hardly definable or not very definite numbers of valency to conventional but quite definite numbers which readily give information on the acid-base and oxidation-reduction properties of elements and can easily be used to find coefficients in the equations of reactions, and conceive the laws of general chemistry.

Chemists avoid using the oxidation number concept in their scientific publications and in routine research. Moreover, the term has not been entered in the authoritative five-volumed Soviet Chemical Encyclopedia. This can probably be explained by that the physical sense of the oxidation number brings chemists back to the old concepts of substance which were characteristic of the past century, when any chemical *individuum* was regarded as a combination of the simplest molecules of the ZnO , Fe_2O_3 , etc. type.

But it was at the third stage of the development of the valency concept that the conditions were provided for the synthesis of the concept of valency as an empirical invariant of the atom properties (or as a quantitative increment of properties: see Chapter 6, Sec. 1) and as a number of bonds in the valence bond method. The former concept originates from the formula of composition of compounds, while the latter from semi-empirical data on the structure of molecules (complexes, single crystals). The basis for the synthesis of these concepts could only be (as is shown in Chapter 7) the molecular orbital method accounting for the chemical composition of particles and (what is important) giving an entirely new (systemic instead of additive) description of their structure.

The 4th stage. This stage of the development of the concept of valency of a bound atom is characterized by the attempts to accomplish the synthesis of concepts. One of the possible approaches to the solution of this problem is the method of calculating valency given in Chapter 7. According to this method, the valency of an atom in a molecule is regarded as a measure of covalency of chemical bonds in which a given atom takes part, or, in other words, as a measure of realization of its valency potentialities with accounting of the redistribution of the electron density of the formed chemical bond depending on the number and the nature of the partners.

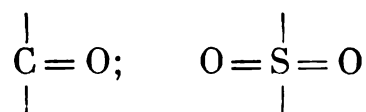
A sufficiently clear physical sense and the mathematic definition of valency of an atom in a molecule thus help establish the quantum-chemical analogue to this classical working concept.

Only first steps have been done in this direction. In future, scientists have to intensify their search for the ways of calculating valencies of atoms in various chemical particles, including complexes, real single crystals, and maybe in surface compounds. Chapter 7, describing these computations and the quantum-chemical analogue of valency of an atom in a molecule, does not emphasize their importance, which however is not less and probably is even greater than that of the classical concept of valency of a bound atom. The role of this analogue has already been defined in brief with reference to scientific papers in the field of catalysis, solutions, and chemistry of the solid state [19-23].

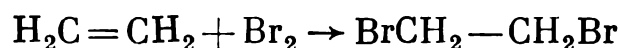
Using the valency concept as a quantitative invariant of properties of elements in a given series of compounds cannot be considered a universal method, but it offers great prospects in the rapidly developing correlation analysis [24].

4. "Free Valencies" of Atoms in Molecules

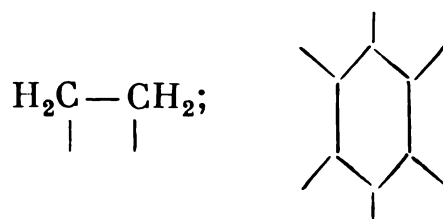
The first concepts of free valencies of atoms in molecules were formulated by Butlerov [4, p. 71-73] who admitted the existence of unused or "incompletely used" affinities of carbon in CO molecules and even in CH_2 [4, p. 77]. On the one hand, these concepts explained variable valency as a different degree of mutual saturation of affinities (see Chapter 2), and on the other hand they became a theoretical foundation for clearly standing out reactivity of all apparently unsaturated compounds:



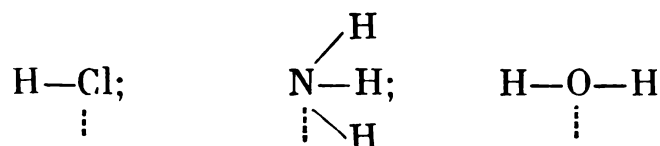
It is interesting to note that despite the unanimously acknowledged "unsaturated character" of olefins, their chemical activity in addition reactions



before the 1890s was not, as a rule, explained by free valencies of carbon. The only exception were few works in which tervalency of carbon in olefins and benzene was admitted:

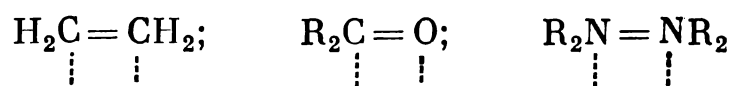


Late in the 1880s and early in the 1890s, Armstrong and Pickering [25, 26] first used the term "residual", i.e. incompletely used affinity of atoms in saturated molecules of some active compounds

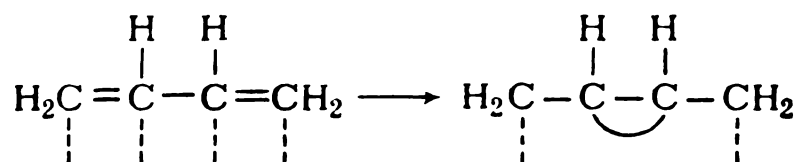


which can be added to other compounds to form complexes NH_4Cl and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Thiele arrived at the idea of residual affinity, as applied to organic compounds, in 1899 [26]. He suggested that the activity of unsaturated molecules could be explained by the presence of partial valencies in atoms which form multiple bonds:

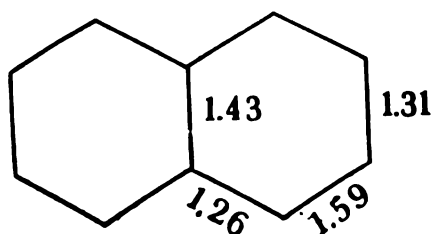


According to Thiele, partial valencies of the adjacent atoms in diene compounds saturate each other; this explains the activity of atoms in positions 1, 4:

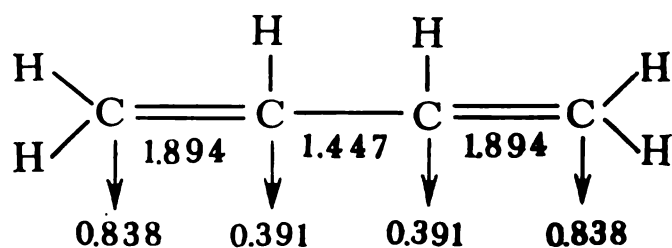


Thiele's ideas lay the foundation for many theories of "affinocapacity", which turned to be an important working tool in explaining and prognosing in synthetic organic chemistry up to the 1930s of our century [28].

Later, according to Coulson [2], the quantum-mechanical variant of the Thiele theory of partial valencies appeared in quantum chemistry. Proceeding from the opinion that the carbon-carbon bonds in benzene are intermediate, in their character, between the ordinary and double bonds, we must, according to Coulson, ascribe a fractional order to this bond. Using the valence bond method, we can calculate this order from the weight of Kekulé and Dewar structures in their resonance series. All six bonds in benzene have one and the same order of 1.46, while in naphthalene they are different



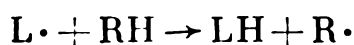
Fractional order of bonds is also described in the molecular orbital method. For butadiene, the bond diagram is as follows:



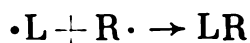
According to Coulson, the bond orders 0.838 and 0.391 in this diagram correspond to Thiele's partial valency or Werner's residual affinity. The bond orders characterize the fixation degree of double bonds, and the charges on the atoms make it possible to determine the most probable points of attack by ions, whereas free valencies to a certain degree indicate how easy the attack by neutral free radicals goes on [2]. The molecular diagrams with "free valencies" of bonded atoms are therefore used for quantitative determination of the reactive potentialities of substances.

Thus, the concept of free valency of bound atoms also has a certain tendency in its development which may not be disregarded. Free valencies of bound atoms are, in the majority of cases, characterized by fractional numbers expressing (like spin-valency values) the reactive potentialities of atoms, i.e. the degree of unpaired state of the outer electrons.

The concept of free valencies of bound atoms has been widely used in the theories of chemical kinetics and heterogeneous catalysis which consider any solid body as a certain kind of a polyradical capable of initiating kinetic chains through the interaction with saturated molecules



as well as of terminating them by capturing and recombining free radicals



where L is the crystal lattice of a solid body [29-31].

5. Valency Theories

Analysis of the development of the valency concepts brings us to very interesting conclusions.

The *first* and the main conclusion is that, from the very first steps of the formation of the valency concept, and in its further development, we can trace two alternate ways:

(1) deepening and enriching the concepts which regard valency as certain individual characteristics of atoms of any given chemical elements, and

(2) widening the concepts of valency to its factual identification with chemism in general.

The *second* conclusion is that the development of the concepts of valency which regard it as individual characteristic of a chemical element leads to differentiation of the very concept of valency to separate into three substantially different concepts, namely:

(1) valency as a reactive power of a free (isolated) atom;

(2) valency as a special structural characteristic of a bound atom or an atom in a molecule;

(3) valency as an incompletely used affinity, or "free valency of a bound atom".

The *third* conclusion is that the concept of the coordination number arises as a direct result of the development of the valency concepts, and it can be regarded as a structural characteristic of the atom in a particle (Chapter 4).

Each of the above mentioned concepts then develops more or less independently in the corresponding theories.

These conclusions are more or less indisputable: they reflect the factual state of the development of the valency theory. These conclusions can be a basis for the solution of one of the most important problems in the development of the valency theory, namely the problem of past and present theories of valency, the problems which these theories should solve. It is quite clear that in connection with the differentiation of the former concept of valency, and creation on its basis of four independent concepts, there may be no general theory of valency at the present time. We shall therefore dwell separately on all those theories each of which uses specific characteristics of these concepts for their own working purposes (explanation, description, prognosis).

Theories of atom reactivity. As has already been said, these are the theories by Kekulé, Delavaud, Abegg, and the theory of spin-valency. They describe valency as a characteristic of potential chemical possibilities of a free atom expressed in whole numbers. Numerous concepts of the reactivity of free atoms in general, and first of all, their ability to form various multi-centre bonds and also less than two-electron two-centre bonds within a wide range of energies (from 2-4 to 200 and over kcal/mole) can be attributed to these theories as well.

The tasks which these theories have performed are enormous. Kekulé's theory was an indispensable precursor for the creation of the theory of chemical structure as the theory of chemical bond. The theories by Delavaud, and later by Abegg, promoted the advance of chemistry towards the modern theory of Periodic system of elements.

The spin-valency theory has disclosed the physical sense of affinity, units of affinity, and valency, as factors which are responsible for the mechanism of chemical aggregation of atoms in a particle of a compound.

But despite the fact that these theories have solved many important problems and the spin-valency theory is still effective at the present time (and shows the tendency to a further development) all these theories are limited by the functions of the electron structure of only outer shells of the atoms. They are therefore only steps leading to a more general theory of the reactivity of free atoms as a part of the theory of the Periodic system of elements.

In fact, the theory of the Periodic system of elements is first of all important to chemists by that it can, to a certain degree, determine various periodically changing characteristics of elements [32] from the structure of atoms. Earlier we discussed only the structure of the outer electron shells of atoms and the consequences that it bears on their spin-valency and the donor-acceptor possibilities. But the reactivity of the atom does not depend only on the structure of its outer shell. The important sign of the atom reactivity is individual chemical characteristics of separate chemical elements which show first of all through the metallic or non-metallic activity. And the latter depends not only on the structure of the outer electron shells but on the structure of the atom as a whole, viz., on the nucleus charge, the quantity and state of electrons in all layers, and on the atomic radius [32].

The general structure of the atom also determines such important (for their chemism) parameters as the ionization energy, affinity for the electron, and electronegativity. These properties of the atoms determine all important chemical aspects of the molecule structure: length and energy of paired interatomic bonds, degree of delocalization of bonds, charges on the atoms, involvement of unpaired electron atomic orbitals into molecular orbitals (free valencies of bound atoms, according to Coulson), etc. [32, p. 107-203].

It is quite clear that any chemical properties of atoms show themselves only in the interatomic interactions, i.e. in the formation of molecules. These properties can therefore most adequately be described on the basis of the study of the existing chemical bonds. But we are not interested in the description of the properties *post factum*; what is interesting to us is the determination (to a certain degree, deductive derivation) of the reactive potentialities of atoms from the data supplied by the Periodic system theory. Our possibilities in this respect are considerable, and they will be more effective in future. The way to discover new possibilities is the further study of the properties of atoms by the properties of molecules.

Theories describing the valency concept as a characteristic of the atom in a molecule. The concept of valency as a characteristic of an

atom in a molecule, connected as it may be with the concept of spin-valency, and its quantitative expression coinciding with that of spin-valency, under all conditions is already a structural characteristic of an element in a new system. It may function therefore along with other structural parameters, such as the atom charge, electronegativity, etc., in various structural theories.

While spin-valency and other reactive potentialities of a free atom only depend on the structure of a given atom, the valency of an atom in a molecule also depends on the valency potentialities of a given atom and on how these potential possibilities are realized in its interaction with all other atoms forming a molecule, i.e. on the surroundings responsible for the classical interatomic effects, or the quantum-mechanical conversion of the atoms into a single system of nuclei and electrons.

Chapter 7 shows that it is possible to find a quantum-chemical analogue to the classical concept of valency of an atom in a molecule. The magnitude of this value can be calculated and the physical sense of the very concept of valency can be disclosed to correlate it with the spin-valency concept without identifying it with the latter. This helps better understand the properties of atoms in molecules compared with the ideal classical model which regarded valency as invariant properties of elements. Chapter 7 also shows that the real values of these properties are in the general case different from spin-valency and can, in principle, be expressed by numbers other than whole.

It follows therefore that quantum-chemical calculations of atom valencies in molecules can determine the degree of conservation and hence the degree of loss of the Mendeleev chemical specificity of elements as a degree of their invariance in the transition from one compound to another. These possibilities can turn into a powerful working tool of structural chemistry, because new prospects for quantitative assessment of the "mutual interatomic effects" can be revealed here.

Theories using the concept of free valencies of bound atoms. It is unnecessary to characterize here the relative simplicity and graphicalness of models of free valencies of bound atoms. The modern quantum chemical literature deals with this question in detail [1, 2]. These are the concepts and models of structural chemistry, and more particularly, of the VB and MO methods. The models are important not only for the description and prognosis of molecule reactivity but also for the explanation of chemical properties of well-known compounds for pedagogical purposes [33].

It is difficult to predict the way along which the concepts of free valencies of bound atoms will develop. It is only possible to say that the tendencies of this development can easily be traced in almost the entire history of structural chemistry and there are no hints that this development will meet with unfavourable prospects.

“Theories of valency” as theoretical chemistry on the whole. In Chapter 1 we mentioned that there exist such theories. Their typical illustrations are books by Coulson [2] and Murrell, Kettle and Tedder [1]. These theories are a direct reflection of one of the tendencies in the development of the valency concept where valency is regarded as everything that is connected with chemism.

Is it lawful to extend the concept of valency to such wide limits? It is difficult to give a simple answer, because there are numerous facts in favour of and against such an expansion. The argument for this expansion is the unitary principle of chemism, because all numerous types of chemical bond are after all only manifestations of one specific type of interaction between material particles, viz., chemical interaction, which can be accomplished: between certain particles (nuclei and electrons), within very limited range of distances (10^{-8} cm), and under the influence of the general tendency of lowering of full energy of the system by quite definite values (10 - 10^2 kcal) by the action of quite definite factors (exchange type; special case of electrostatic attraction). The unity of the object also requires the unity of its ideal reflection, i.e. unified theory. The “theory of valence” by Coulson, Murrell, and others meets this requirement. But the entire theoretical chemistry meets this requirement as well. And here arise the arguments *against* an unreasonably loose interpretation of the theory of valency. Theoretical chemistry reflects its material object to find in this object the unity of the general, special, and singular. The general in this object is chemism, i.e. the chemical interaction. The special and singular are numerous chemically individualized quantum-mechanical systems which make up a certain hierarchy: atoms, simplest molecules, complicate molecules, complexes, solid particles, microheterogeneous systems, biopolymers and bioregulators, etc. The unified object of chemistry is therefore a certain section of that general hierarchic scale of ranks which is characteristic of the entire material organization on the whole. And chemistry, as the reflection of this section, is therefore differentiated to put forward separate theories for each level of chemical systems. And therefore the authors of the “Valence Theory” [1] dedicate special chapters in their book to describe these independent theories: “The foundation of atomic theory” (Chapter 1), “Ligand-field theory” (Chapter 13), and “ π -Electron theory of organic molecules” (Chapter 15). They call the quantum-mechanical description of chemical bonds as the “valence bond method”, “the atom in a molecule method”, etc., and thus discuss independent concepts of chemical bond in molecules, which are often called “theories” (see e.g. Ref. [34]). The “Valence Theory” thus appeared to comprise the theories of atom, theories of molecules, theories of solid body, and even kinetic theories.

But the inconvenience of identifying the valency theory with the entire theoretical chemistry does not only consist in this inclusion of

theories inside a theory. The disadvantage of this identification is also that this has led to complete disappearance of the concrete concept of valency. From the book by Coulson entitled "Valence" [2] and the book "Valence Theory" by Murrell *et al.* [1], it is impossible to conceive what valency actually is unless we identify it with chemism.

But the first chapters of these books formulate the concrete objects of the valency theory, though... of the valency theory in its classical meaning (or also in the spirit of the spin-valency theory), as a theory of potential reactivity of a free atom.

The authors of Ref. [1] assume that the valency theory must meet the following requirements:

(1) it should explain why, in general, some atoms can and others cannot be combined into compounds (for example, the reaction $2\text{H} \rightarrow \text{H}_2$ can be accomplished while the reaction $2\text{He} \rightarrow \text{He}_2$ cannot) and can be used to calculate the energy of bond;

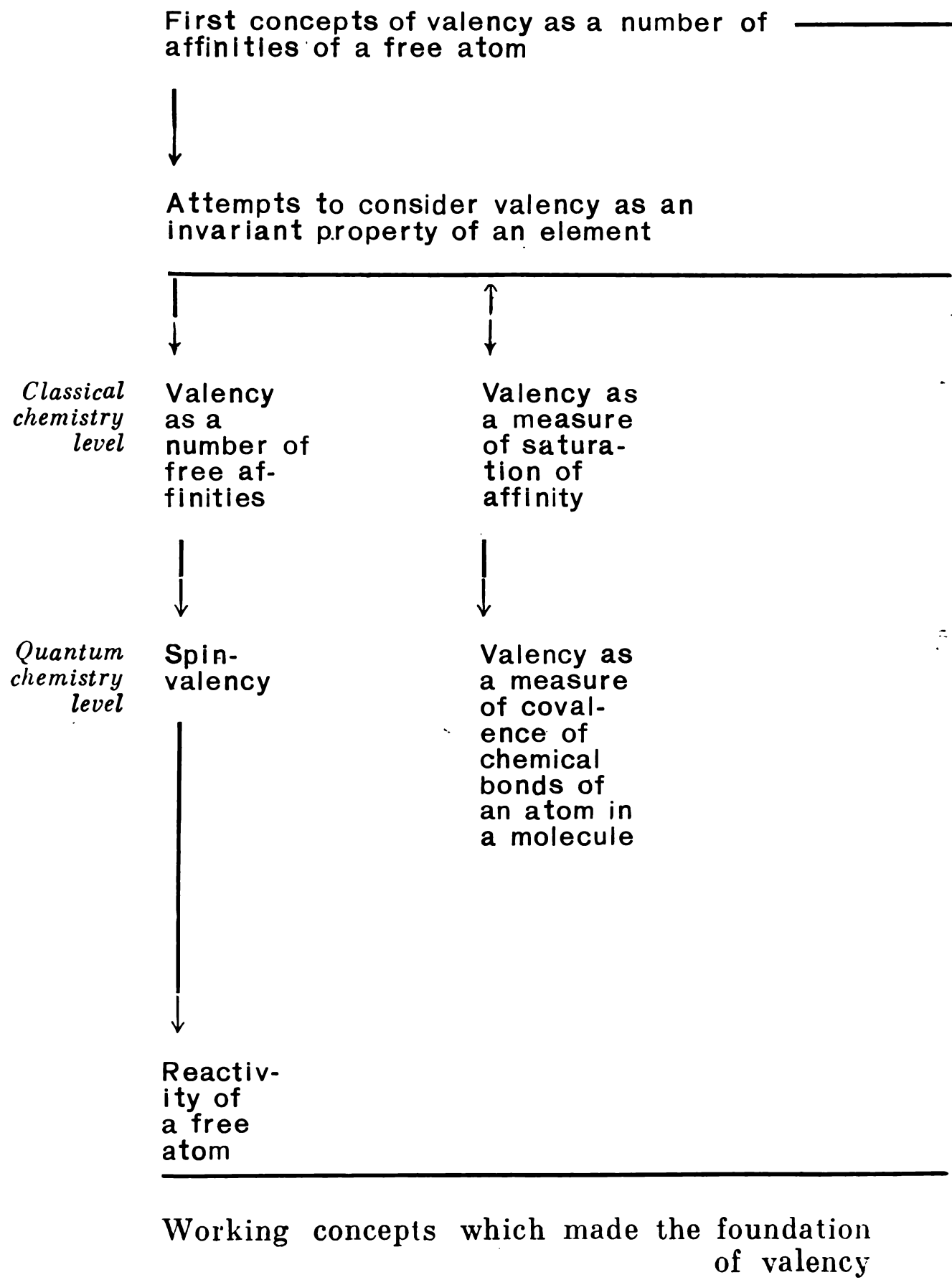
(2) it should explain why atoms are combined in definite proportions (for example, CH_4 is a stable molecule, while CH_3 , CH_5 , etc. are unstable);

(3) it should explain, and wherever possible predict, lengths of bonds and angles between them.

It is easy to see that those special theories which describe reactivity of atoms can to a certain degree answer these questions. The third question can only be answered to that degree of certainty to which our knowledge of the potentialities of each atom can help clear out the degree of their realization in the atomic interaction. But the interaction is a very complicate process which depends on the interaction of the partners, and the knowledge of valency potentialities is not therefore sufficient to predict the lengths and angles of bonds. A definite theory of chemical bond must function here. For example, atom of lithium can form chemical bonds because of its structure ($1s^2 2s$), i.e. at the expense of one $2s$ -electron in the valent shell. This differs lithium from atoms of any other element, e.g. from the atoms of Be, B, etc. But how the combining power of this $2s$ -electron will be realized, depends on the partners in the reaction and on the reaction conditions. A lithium atom can combine with another lithium atom to form the Li_2 molecule by sharing two s -electrons. The length of the $\text{Li}-\text{Li}$ bond is 2.67 Å. But as the same atom interacts with n atoms of lithium, a single crystal is formed whose bonds are formed by sharing ns -electrons into the "electron gas". In this case the atom of lithium is connected with eight adjacent atoms, the interatomic distance being 3.03 Å.

Thus, the information on the ways of interaction or on the types of chemical bond can be obtained from the theory of chemical bond, while the answer to the questions, why some atoms can and others cannot be combined into compounds, and why atoms are combined in

Evolution
of valency concept



definite proportions can be given by the "theory of atom", i.e. the theory of the Periodic system of elements, the theory of atomic structure. These latter theories are the "first chapters", or the starting point of modern theoretical chemistry. These theories give a concrete definition to valency as a concept expressing the dependence of the reactive possibilities of atoms on their structure, and on their position in the Periodic system. Here the valency concept is the working theory. But in the "expanded" theory of valency by Murrell, Kettle, and Tedder this concept has practically ceased to exist.

Thus our historico-chemical essay produced a more or less comprehensive picture of the development of the valency theory. For the purpose of graphicalness, this picture can be represented as a diagram, and the closing chapter of this book is the explication of this diagram.

References

1. Murrell, J. N., Kettle, S. F. A., Tedder, J. M., *Valency Theory*, London-N.-Y.-Sydney, 1965.
2. Coulson, C. A., *Valence*, Oxford University Press, 1961.
3. Kuznetsov, V. I., *Continuity, Unity, and Minimization of Knowledge: Fundamental Features of Scientific Method*; in the book "Materialistic Dialectics and Methods of Natural Sciences", Nauka, Moscow, 1968, p. 341 (in Russian).
4. Butlerov, A. M., *Collected Works*, vol. 1, Academy of Sciences Press, Moscow, 1953 (in Russian).
5. Tatevskii, V. M., *Quantum Mechanics and Theory of Molecular Structure*, Moscow University Press, 1965 (in Russian).
6. Tatevskii, V. M., *Classical Theory of Molecular Structure and Quantum Mechanics*, Khimia, Moscow, 1973 (in Russian).
7. *Centenary of the Theory of Chemical Structure*; Collected papers by A. M. Butlerov, A. S. Couper, A. Kekulé, and V. V. Markownikoff, USSR Academy of Sciences Press, 1961 (in Russian).
8. Bykov, G. V., *History of Electronic Theories of Organic Chemistry*, Academy of Sciences Press, Moscow, 1963, p. 94 (in Russian).
9. Veselov, M. G., *Elementary Quantum Theory of Atoms and Molecules*, 2nd enl. ed., Fizmatgiz, 1962, p. 32 (in Russian).
10. Trifonov, D. N., *Quantitative Interpretation of Periodicity*, Nauka, Moscow, 1971 (in Russian).
11. Trifonov, D. N., *On Quantitative Interpretation of Periodicity*, Nauka, Moscow, 1971, p. 159 (in Russian).
12. Volkenshtein, M. V., *Structure and Physical Properties of Molecules*, Academy of Science Press, Moscow-Leningrad, 1955 (in Russian).
13. Pimentel, G. C., Spratley, R. D., *Chemical Bonding Clarified Through Quantum Mechanics*, San-Francisco, Cambridge, London, Amsterdam, 1970.
14. *Course in Chemistry*, Part 1, Vysshaya shkola, Moscow, 1971 (in Russian).
15. Krasovitskaya, T. I., *Electronic Structures of Atoms and Chemical Bond*, Prosveshchenie, Moscow, 1972, p. 129-132 (in Russian).
16. Gray, H. B., *Electrons and Chemical Bonding*, N.-Y.-Amsterdam, 1964.

17. Charkin, O. P., *ZhVKhO im. Mendeleeva*, 1972, vol. 17, p. 251-258 (in Russian).
18. Syrkin, Ya. K., *Usp. Khim.*, 1959, vol. 28, p. 903-920 (in Russian).
19. Krylov, O. V., *Catalysis with Non-metals*, Khimia, Leningrad, 1967 (in Russian).
20. Kuznetsov, V. I., *Development of the Theory of Catalysis*, Nauka, Moscow, 1964 (in Russian).
21. Korneyev, N. N., Popov, A. F., Krentsel, B. A., *Complex Organometallic Catalysts*, Khimia, Leningrad, 1969 (in Russian).
22. Lilich, L. S., Mishchenko, K. P., *Periodic Law and Theory of Solutions*, in the book "Centenary of the Periodic Law of Chemical Elements", Nauka, Moscow, 1969, p. 302 (in Russian).
23. Cotton, F. A., Wilkinson, G., *Advanced Inorganic Chemistry*, Interscience Publishers, N.-Y.-London-Sydney, 1962.
24. Zhdanov, Yu. A., Minkin, V. I., *Correlation Analysis in Organic Chemistry*, Rostov-on-the Don University Press, 1966 (in Russian).
25. Pickering, S. U., *Ber.*, 1891, Bd. 24, S. 3629-3647.
26. Armstrong, H. E., *J. Chem. Soc.*, 1895, v. 67, p. 97-145.
27. Thiele, I., *Lieb. Ann.*, 1899, Bd. 306, S. 87-142.
28. Ingold, C. K., *Structure and Mechanism in Organic Chemistry*, N.-Y., 1953.
29. Voevodsky, V. V., Volkenshtein, F. F., Semenov, N. N., in the book "Problems of Chemical Kinetics, Catalysis, and Reactivity", Academy of Sciences Press, Moscow, 1955, p. 423-440 (in Russian).
30. Semenov, N. N., *Some Problems of Chemical Kinetics and Reactivity*, Academy of Sciences Press, Moscow, 1958 (in Russian).
31. Volkenshtein, F. F., *Electronic Theory of Catalysis with Semiconductors*, Fizmatgiz, Moscow, 1960 (in Russian).
32. *Periodic Law and Atomic Structure*, Atomizdat, Moscow, 1971 (in Russian).
33. Nesmeyanov, A. N., Nesmeyanov, N. A., *Fundamentals of Organic Chemistry*, vol. 1, MIR Publishers, Moscow, 1976.
34. *Modern Quantum Chemistry*, Edited by O. Sinanoglu, v. 1, v. 2, Academic Press, N.-Y.-London, 1965.

Author index

- Abegg, 26, 80, 119-121, 251
Alexeyev, 129, 236
Ampere, 60
Anschütz, 39, 40, 43
Aria, 144
Armstrong, 26, 98, 151, 160-162, 249
Avogadro, 34, 50, 68
- Baranovskii, 162
Barka, 124
Bazarov, 86, 91, 92
Belov, 14
Berthollet, 83
Berzelius, 34, 36, 49, 50, 68, 87, 91, 179
Bethe, 178
Blomstrand, 54, 61, 62, 71, 90, 91, 97, 102, 104
Bodländer, 119-121
Boer, 114
Bohr, 123, 124, 126
Bokiy, 14
Borisova, 151
Boyle, 42
Bregman, 68
Brown, 55-57, 232
Butlerov, 23, 24, 29, 41, 47-53, 62, 63, 67, 69-71, 82, 85, 94, 233-235, 240, 241, 248
Bykov, 43
Byron, 79
- Cannizzaro, 39, 40
Caylay, 127
- Charkin, 244
Chichibabin, 67
Chugaev, 24, 47, 77, 78
Claus, 100, 101
Clifford, 127, 129, 236
Cooke, 45
Coulomb, 176, 215, 221
Coulson, 27, 196, 205, 233, 239, 241, 249, 250, 252, 254, 255
Couper, 40, 45, 48, 51, 52, 54, 56, 64, 67, 86, 232
- Dalton, 9, 34, 49, 83, 137, 148
Davy, 68
Day, 114, 115
Delavaud, 26, 53, 58-63, 69, 236, 251
Del Re, 207
Dewar, 129, 134, 206, 249
Drude, 120
Dumas, 38, 42, 76
- Erlenmeyer, 55-58, 69, 71
- Fajans, 114
Faraday, 111
Fock, 178, 186, 190, 191, 212
Fortune, 160, 162
Foster, 64
Friedel, 64
Frankland, 24, 35-57, 62-65, 69, 111, 112, 232, 234
- Gauss, 191
Gerhardt, 35-51, 75

- Gibbs, 72
Gillespie, 203
Gordan, 129, 236
Grinberg, 113
- Hartree, 178, 186, 190, 191, 212
Heitler, 20, 21, 130, 178, 195, 244
Hellmann, 193
Helmholtz, 80, 207, 208
Higgins, 56
Hofmann, 36, 45, 47, 48, 156, 204, 206
Holleman, 47
Hückel, 198, 207
Hund, 170
Hurley, 203
- Jahn, 170
Johnson, 212
Jones, 203
Jørgensen, 97
- Kaemmerer, 90
Kant, 212
Kaplan, 196
Kedrov, 75, 148
Kekulé, 12, 24, 26, 38-72, 82, 85-96, 102, 129, 132-134, 168, 232-235, 240, 241, 249-251
Kettle, 27, 195, 233, 255, 258
Klaus, 67
Kolbe, 35-39, 41-43, 50
Koopman, 190
Korolkov, 145
Kossel, 112, 113, 114, 119, 123-127
- Langmuir, 125-127, 237
Laurant, 35-37, 44, 45, 50
Lennard, 203
Lewis, 115, 123-127, 150, 237
Lodge, 111, 112
- London, 20, 21, 130, 178, 195, 244
Loschmidt, 54
Lossen, 66, 67, 100, 101
Löwdin, 152
- Magnus, 113, 114
Markownikoff, 55, 71
McWeeny, 186, 190, 192, 206
Mendeleev, 46, 47, 74, 75-83, 95-98, 102, 120, 137, 138, 142, 223, 224, 235, 253
Menshutkin, 11, 24, 47, 75, 206
Meyer, 75, 80, 93-95, 99
Michaelis, 99
Moseley, 124
Mulliken, 178
Murrel, 27, 195, 205, 233, 254, 255, 258
Musher, 216, 217
- Naquet, 54, 61, 85
Nekrasov, 114
Netter, 129
Newlands, 86
- Odling, 35-48, 53, 54, 65
Ostwald, 47
- Parsons, 125
Partington, 56
Pauling, 115, 142
Pearson, 206
Perkins, 151, 160, 161, 162, 249
Pickering, 26, 99
Pople, 203, 207, 208
Proust, 83
- Ramsay, 111
Roscoe, 45
Robertson, 126

- Roothaan, 189-191, 196, 206, 212
Rumer, 150, 193
Russel, 37, 41-48, 62, 63
Rydberg, 125
- Schrödinger, 178, 182, 183
Selbin, 114, 115
Semyonov, 151
Sestini, 65
Shchukarev, 10, 22
Sidgwick, 115
Sizova, 162
Slater, 188, 191-194, 212
Stalo, 45
Stark, 26, 122
Stewart, 151, 161
Study, 129
Sutcliffe, 186, 192, 206
Sylvester, 127, 129, 236
Syrkin, 19, 30, 207
- Tatevskii, 25, 26, 161, 185, 234
Tedder, 27, 195, 233, 254, 258
Teller, 170
Thiele, 26, 29, 30, 54, 74, 122, 249, 250, 257
Thomson, 80, 111, 121, 122
- Van-Arkel, 114
van't Hoff, 26, 80, 99
Van-Vleck, 116, 178
Volkenshtein, 239
- Werner, 26, 67, 80, 85, 90, 100-112, 103, 179, 237, 250, 257
Weyl, 128, 130
Wheeler, 56
Wiberg, 151, 155, 162
Wichelhaus, 45, 64
Wiedemann, 60
Williamson, 35-39, 42-45, 48
Wislicenus, 100
Wolfsberg, 207
Woodward, 204, 206
Wunderlich, 99, 100
Wurtz, 35, 36, 38-40, 43, 54, 58-61, 65, 69, 87-93, 96
- Yatsimirsky, 141, 142
Young, 134
- Zeise, 160, 168

TO THE READER

Mir Publishers welcome your comments on the content, translation and design of this book.

We would also be pleased to receive any proposals you care to make about our future publications.

Our address is:

Mir Publishers

2 Pervy Rizhsky Pereulok,

I-110, GSP, Moscow, 129820,

USSR